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SUMMARY

A series of phenolic-based flat-face charring ablation specimens was tested in a subsonic arc jet at a cold-wall heating rate of 110 Btu/ft^2-sec for periods of time ranging from 30 seconds to 10 minutes. Comprehensive temperature surveys were made within the ablating materials, and the char depths and char character were studied to provide some knowledge of the effectiveness of the charring phenolics as thermal protection materials. The percentage composition of phenolic-nylon, molded of powdered phenolic resin and powdered nylon, was varied systematically. Of the variations tested the composition of 40-percent phenolic—60-percent nylon developed a char layer of reasonably good integrity and provided the longest protection time. The use of phenolic Microballoons as a filler to replace half of the powdered phenolic resin in a basic 50-50 phenolic-nylon composition yielded a lightweight composite which had improved char integrity and which offered a longer protection time when its low density was taken into consideration. The presence of the Microballoons, however, caused accelerated ablation rates and deleterious shape changes. Incorporation of high-temperature fibrous fillers, glass, refractory silica, and zirconia, into the phenolic-nylon yielded slightly more dense materials which developed, in the arc-jet environment, chars of improved integrity and which provided, in the case of refractory silica and zirconia, increased thermal protection time and minimum shape changes. A composite having both Microballoons and refractory silica fiber fillers showed improved thermal protection time but suffered the large shape change apparently inherent with Microballoon-filled materials. The substitution of ammonium chloride or Teflon powder for nylon in the basic phenolic resin composition yielded materials of slightly higher density and inferior thermal protection capabilities.

INTRODUCTION

A comprehensive screening program, reported in reference 1, to evaluate ablating heat-shield materials for manned reentry vehicles has shown that the charring-composite class of ablation materials combines the desirable features of ablation, radiation, and low thermal diffusivity to maintain effectively low temperature on the walls of the occupied area of the vehicle for extended periods of time. In this screening program the candidate ablation materials were fabricated into disk-shaped specimens having thicknesses such that all specimens were of the same weight, and the ablation performance criterion was the time required for an arc-powered air jet to produce a temperature rise of 300° F on the unheated surface of the specimen.

In order to study the performance of these charring ablation materials over a greater temperature range and to determine means of improving this performance, a complementary experimental program was initiated. Using one of the more promising charring ablation materials reported in reference 1 as a reference material, the material formulations were varied systematically and additives were incorporated into the formulations in order to gain some insight into the relative contribution of the various constituents to the overall performance of the ablation material. The formulations were molded to greater thicknesses to afford longer testing times, and a plurality of thermocouples was installed in these thicker specimens to obtain temperature histories within the ablating material. In addition to the temperature variations, studies were made of char thicknesses, char integrity, and shape changes of the ablating materials. The purpose of this paper is to report the results of this investigation.

MATERIALS AND SPECIMENS

Materials

The comprehensive screening program for ablation materials reported in reference 1 showed the relative superiority of a phenolic-nylon composite as a charring ablator. Accordingly, this phenolic-nylon, molded of equal parts by weight of powdered phenolic and powdered nylon, was used as a reference material in the present investigation. In addition to the basic 50-50 phenolic-nylon, a number of other compositions were included in the program to obtain a deeper understanding of the ablating performance of phenolic-nylon.

Various fillers, both a low-density filler and several high-temperature fibrous fillers, were incorporated into the basic phenolic-nylon in an attempt to improve the char integrity and the ablation performance. Other low-temperature gas-producing materials, replacing nylon, were combined with the phenolic resin to study this effect on the char formation. The materials studied in this investigation and the compositions used are categorized as follows: (All compositions listed are in percent by weight. For example, 75-percent phenolic with 25-percent nylon is designated 75-25 phenolic-nylon.)

(1) Phenolic-nylon compositions:
- (a) 100-percent phenolic resin
- (b) 75-25 phenolic-nylon
- (c) 50-50 phenolic-nylon
- (d) 40-60 phenolic-nylon
- (e) 25-75 phenolic-nylon
- (f) 12.5-87.5 phenolic-nylon
- (g) 100-percent nylon

(2) Low-density filler: 25-50-25 phenolic-nylon-Microballoons

(3) High-temperature fibrous fillers:
   (a) 32.5-50-17.5 phenolic-nylon-roving glass fibers
   (b) 32.5-50-17.5 phenolic-nylon-refractory silica fibers
   (c) 32.5-50-17.5 phenolic-nylon-zirconia fibers

(4) Low-density plus high-temperature fibrous fillers: 22.5-45-22.5-10 phenolic-nylon-Microballoons-refractory silica fibers

(5) Low-temperature ablators to replace nylon
   (a) 50-50 phenolic-ammonium chloride (NH_4Cl)
   (b) 50-50 phenolic-Teflon

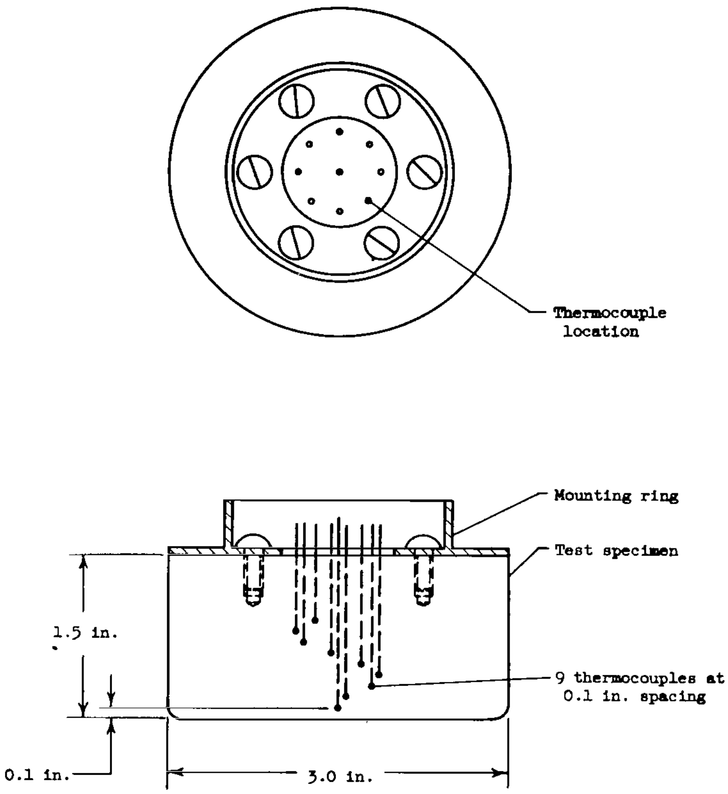


Figure 1.- Details of specimen, mounting ring, and thermocouple location.

The phenolic resin used in these formulations was a general purpose resin. The powdered nylon was a commercial grade. The 100-percent nylon specimen was a solid white molded block as purchased from a commercial plastics fabricator. It is recognized that special phenolics have been developed specifically for high-temperature or ablation purposes and for more amenable blending with polyamide resins. However, the general purpose phenolic resin was selected to keep the results of this investigation consistent with the results of reference 1, which used the same general purpose phenolic. It is anticipated that the special phenolics tailored for better ablation performance will show improved performance over that reported herein.

Specimens

The phenolic-nylon specimens and all the variations listed were molded under the same temperature and pressure conditions except those specimens containing the phenolic-Microballoons. These specimens were molded at a reduced pressure to avoid the possibility of crushing the Microballoons. All specimens were molded oversize and were machined to the dimensions shown in figure 1.

The test specimen configuration was a flat-face cylinder of 3-inch diameter and 1.5-inch thickness. The specimens were mounted on a brass adaptor ring to permit attachment to the 3-inch-diameter water-cooled sting described in reference 1. At least 2 specimens of each material were instrumented with 9 No. 30 chromel-alumel thermocouples imbedded in the specimen at nominal 0.1-inch intervals from the heated surface of the material as shown in figure 1. The thermocouple wires were beaded immediately below the insulation, and were inserted into 0.070-inch drilled holes containing an epoxy cement. After the curing of the cement, the specimens were X-rayed to verify the location of each thermocouple.

TEST EQUIPMENT

The experimental study of the effectiveness of the charring ablators was performed in the 2,500-killowatt arc jet (fig. 2) located at the Langley Research

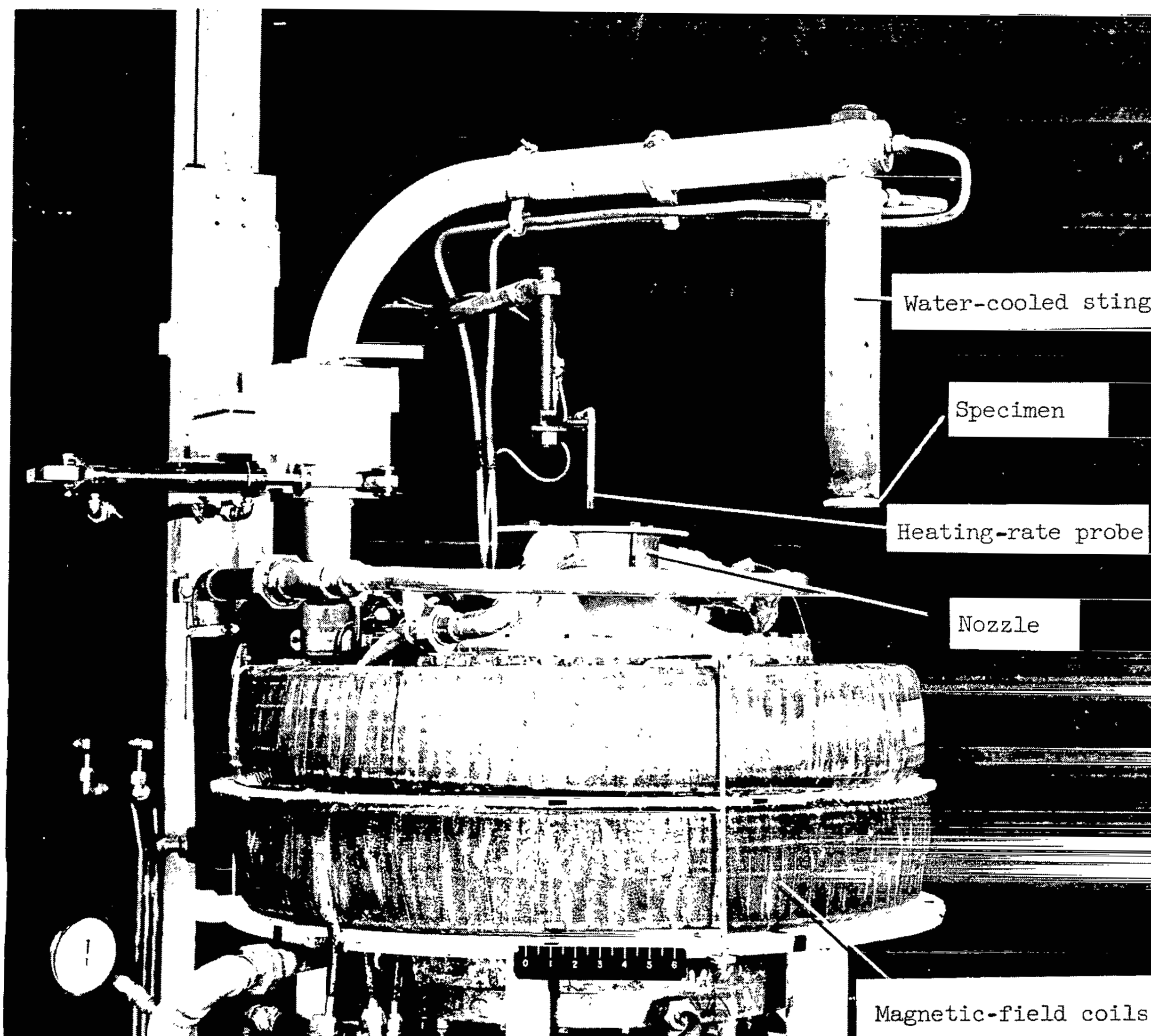


Figure 2.- 2,500-kilowatt arc jet. L-61-3423.1

Center. This facility utilizes concentric annular water-cooled copper electrodes and a water-cooled copper arc chamber. Compressed air introduced at the bottom of the arc chamber is heated by passage through the arc region. The heated air exits through a 4-inch-diameter water-cooled subsonic nozzle and is directed to the test specimen. The conditions provided for these tests in the 2,500-kilowatt arc jet are as follows:

Heating rate (to 3-inch-diameter flat-face specimen)	110 Btu/ft^2-sec
Stream enthalpy	3,000 Btu/lb

The 2,500-kilowatt arc jet is equipped with a hydraulically operated specimen inserter for inserting and retracting the specimen from the jet.

The performance of the jet was monitored in each test by a 3/8-inch-diameter heating-rate probe similar to that described in reference 2. The heating rate measured by this probe was corrected to that of the 3-inch-diameter specimen size by using a correlation factor previously determined from a 3-inch-diameter calorimeter. In addition, the gas temperature of the jet was measured spectographically by the copper line method described in reference 3.

A motion-picture camera operating at either 16 or 24 frames per second was used to record specimen appearance and surface regression. Specimen surface temperatures were measured with an optical pyrometer. Thermocouple temperatures within the specimen were recorded oscillographically.

TEST PROCEDURE

The specimens to be tested were mounted on the 3-inch-diameter water-cooled sting with the specimen inserter in the retracted position. The arc jet was started and the airflow rate was stabilized at 0.35 pound per second. The 3/8-inch-diameter heating-rate probe then was inserted into the jet, and the heating rate was recorded for approximately 20 seconds. Then the motion-picture camera was started and the specimen was inserted quickly into the jet. After the desired specimen exposure time had been attained, the specimen was retracted from the jet, the heating-rate probe was reinserted to record the heating rate for approximately 10 seconds before the jet operation was terminated. Exposure times were varied in 1-minute intervals from 1 to 10 minutes, depending on the regression rate or shape change of the material, to develop a series of increasing char depths. In addition, a number of 30-second exposures were made to study the initial char formation.

After the tests, the specimens were photographed and were removed from the mounting ring for weighing and measuring. The specimens were then sectioned to permit measurement of the char depth and observation of the char structure. The total char depth was measured by a scale graduated to 0.01 inch.

RESULTS AND DISCUSSION

This investigation comprises a number of material composition variations. To facilitate a discussion of these results, the materials are categorized according to the primary effect evaluated in each group as follows:

(1) Ablation characteristics of 50-50 phenolic-nylon

(2) The effect of varying the phenolic-nylon formulation

(3) The effect of a low-density filler

(4) The effect of high-temperature fibrous fillers

(5) The effect of low-density plus high-temperature fibrous fillers

(6) The substitution of other low-temperature gasifiers for nylon

The materials tested and the results of these tests are summarized in table I. The cold-wall convective heating rates, measured by the 3/8-inch-diameter calorimeter and corrected for size to that of a 3-inch-diameter flat-face specimen, averaged 110 Btu/ft^2-sec. The values for all tests were within a ±6-percent scatter band. The enthalpy of the arc jet stream was 3,000 Btu/lb based on the measured stream temperature. The data obtained from the tests consist of recorded thermocouple temperature histories, optical pyrometer surface temperature readings, material and char thicknesses, surface regression rates, and visual qualitative observations of the materials under test.

Ablation Characteristics of 50-50 Phenolic-Nylon

The basic material used in this investigation was a molded phenolic-nylon composed of equal parts of powdered phenolic resin and powdered nylon. Thirteen specimens of this basic 50-50 phenolic-nylon were tested for various exposure times from 30 to 416 seconds.

Temperature histories.- A typical set of temperature histories obtained from one specimen of 50-50 phenolic-nylon is shown in figure 3. The temperature histories recorded from the 9 thermocouples within the specimen are shown as solid lines, and the char surface temperature rise, as measured by the optical pyrometer readings by assuming an emissivity of 1, is shown by the test points connected by a dashed line. The location of each thermocouple with respect to the original heated surface of the specimen is indicated by the dimensions adjacent to the curves. No attempt has been made in this paper to correlate the measured specimen surface temperatures with the equilibrium temperature corresponding to the convective cold-wall heating rate because such an analysis is beyond the scope of this investigation and would not contribute significantly to the material comparisons presented.

Protection time.- The time intercepts corresponding to a temperature rise of 300° F were read from the temperature histories (fig. 3) for each thermocouple

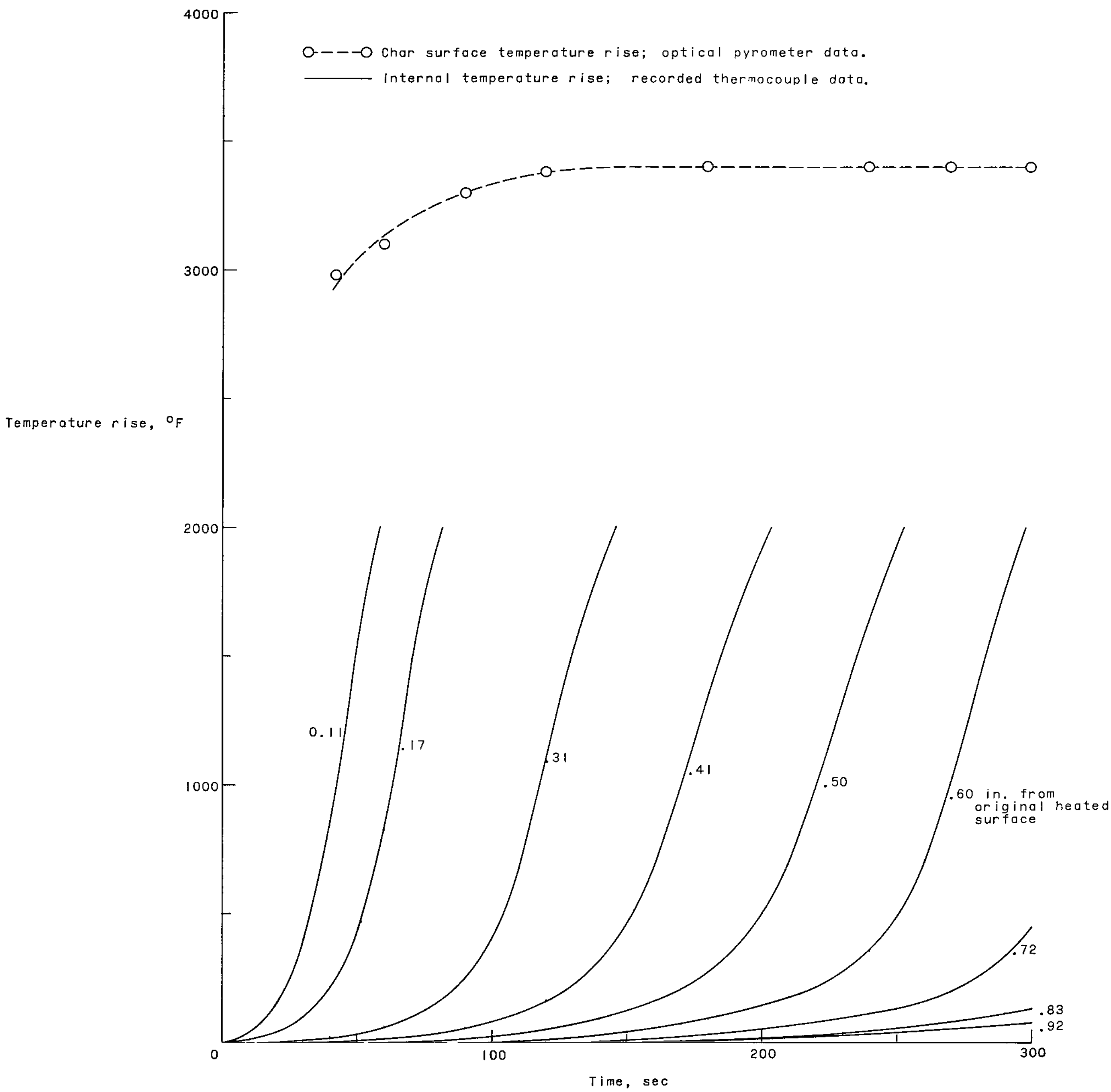


Figure 3.- Temperature histories for a typical test of molded phenolic-nylon of 50-50 composition.

location. The thermocouple locations, measured as distances from the original heated surface of the specimen, were plotted against these time intercepts in figure 4. The test points shown are for all the tests of 3-minute duration or longer made on instrumented specimens of 50-50 phenolic-nylon. A curve was faired through these points and this curve indicates the thickness of heat-shield material required to protect a body for a specified time against a 300° F temperature rise in the test environment. Curves of this type are used in the ensuing discussion to compare the performance of the charring ablation materials of this investigation.

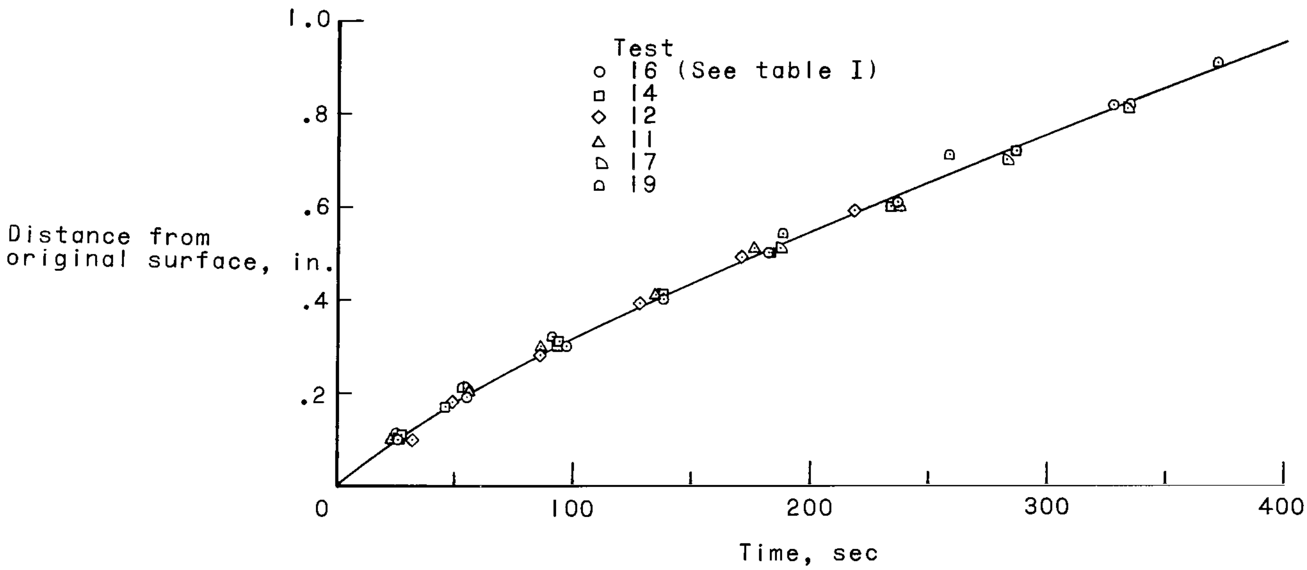
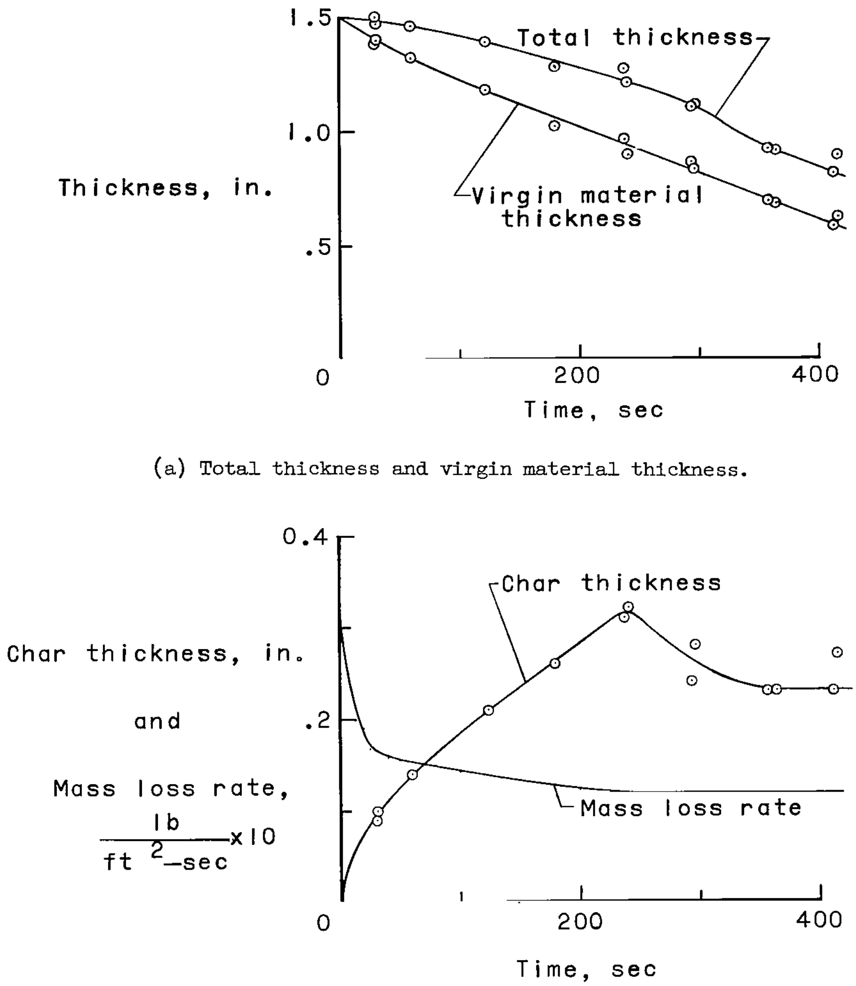


Figure 4.- Variation of material thickness with protection time to 300° F based on thermocouple temperature histories. Material, 50-50 phenolic-nylon.

Char thickness.- The measurements of the sectioned specimens of 50-50 phenolic-nylon are plotted in figure 5(a). Both the total thickness and virgin material (uncharred material) thicknesses are shown. The char thickness measurements are plotted in figure 5(b) and can be seen in figure 6 in which eight of the sectioned specimens are shown arranged in order of test time from 30 to 416 seconds. The original specimen size and shape are shown by the line drawn around the specimen of 416-second exposure. It will be noted that the char thickness does not continue to increase with time, but rather it attains a maximum thickness at about 3 to 4 minutes and then decreases. The decrease in char thickness after several minutes of exposure is believed to be due to a change in oxidation process. However, the reason for the change in oxidation rate has not been determined. It may be due to possible shunting of the pyrolysis gases to the side areas of the specimen or some other phenomenon resulting in a change in oxygen concentration at the front surface of the specimen. (The mass loss curve (fig. 5(b)) is discussed later.)

Character of char.- The char layer formed on the 50-50 phenolic-nylon in the 2,500-kilowatt arc jet consisted of a series of bonded columns of approximately 1/16-inch diameter. The columns were oriented perpendicular to the original



(a) Total thickness and virgin material thickness.

(b) Char thickness and mass loss rate.

Figure 5.- Ablation and char-thickness histories for molded phenolic-nylon of 50-50 composition.

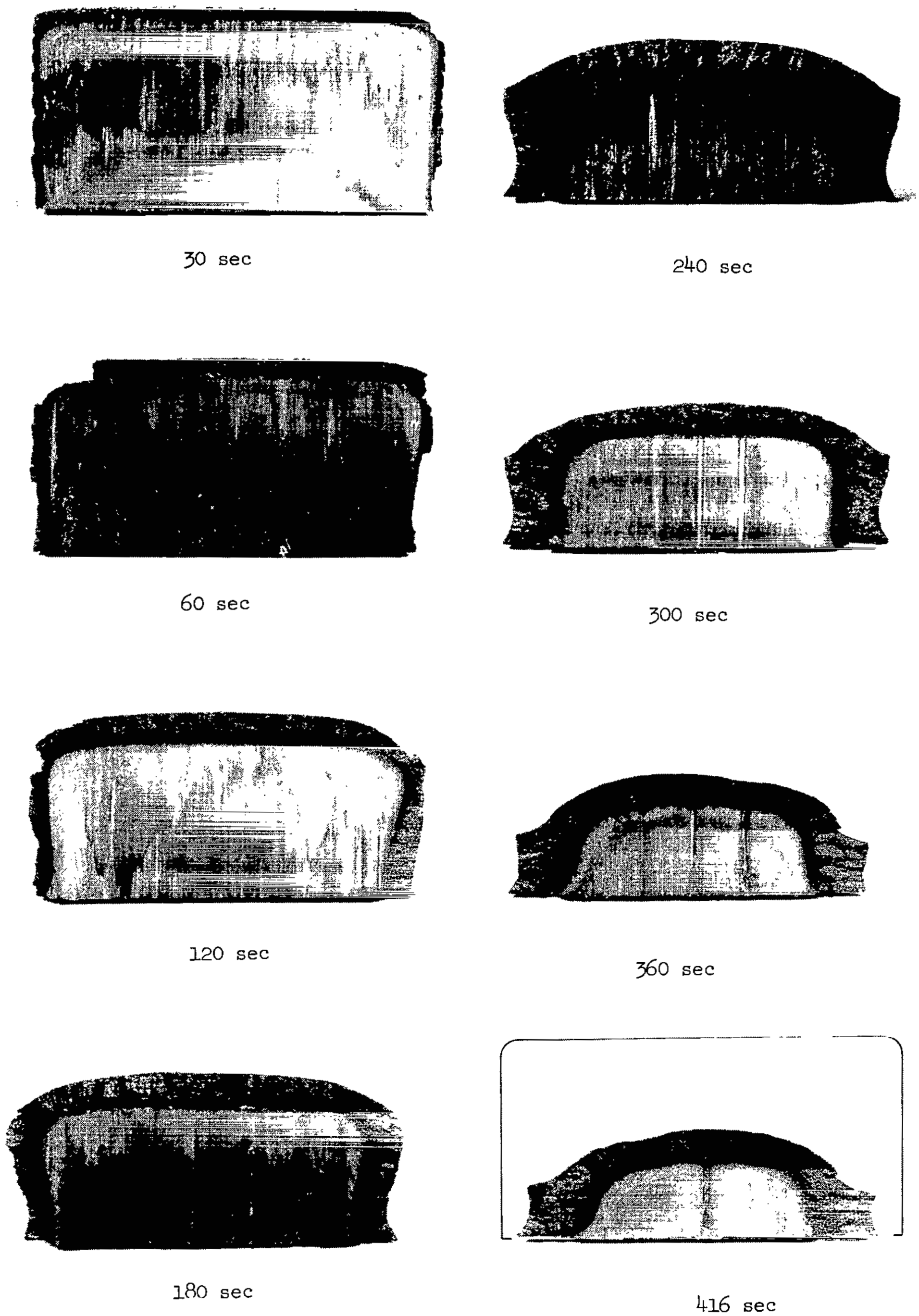


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Figure 6.- Sectioned specimens of 50-50 phenolic-nylon tested in 2,500-kilowatt arc jet for exposure times from 30 seconds to 7 minutes.

specimen surface. The individual columns were rather hard and resembled coke in appearance. The bond between adjacent columns was sufficient to give the char layer some degree of integrity. Once the char layer was cut, however, it was possible to pick off individual char columns. The outer surface of the char was hard. On sectioning the specimens after test the power saw blade threw off a moderate shower of sparks when this hard outer layer was cut. This condition would indicate the possible presence of a carbide on the surface of the char.

Between the columnar char layer and the virgin material there was a layer of rather soft, friable, sooty char. This layer, called the pyrolysis zone, was responsible in many cases, particularly the tests of 5-minute duration or longer, for the separation of the char layer from the virgin material. (See fig. 7.) It is not known whether this friable layer developed during the exposure to the hot gas environment or whether it developed during the brief cool-down period after the specimen had been removed from the jet.

A char of good integrity should, to perform satisfactorily in the heat-shield application, be reasonably well self-bonded - that is, the individual columns should adhere well to themselves - and should adhere well to the virgin material. The char formed on the 50-50 phenolic-nylon in these tests, then, fulfills only one of these two requirements. The char layer is well bonded as evidenced by the fact that the char layer is in one piece as shown in figure 7 and can be handled without breaking up. However, the loose friable layer adjacent to the virgin material does cause the char to separate from the virgin material.

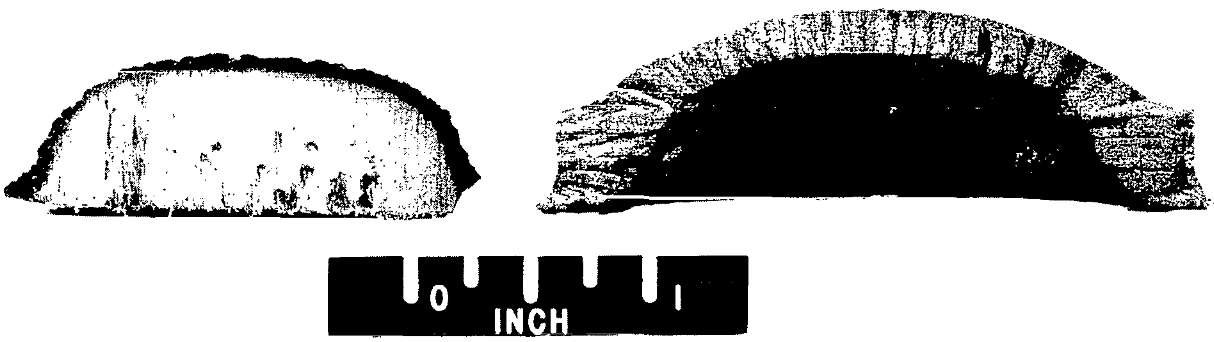

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Figure 7.- Separation of char layer due to poor bonding to virgin material. Specimen material, 50-50 phenolic-nylon; exposure time, 7 minutes.

<u>Mass loss rate</u>.- The mass loss rate for the 50-50 phenolic-nylon was computed from the slopes of the curve faired through virgin material thicknesses plotted in figure 5(a). The resulting mass loss rate curve is shown in figure 5(b). It will be noticed that the mass loss rate attains a steady-state value after 220 seconds. This is also approximately the time at which the char thickness attains its maximum value. By comparing the mass loss rate with the char surface temperature rise shown in figure 3, it is seen that the mass loss rate is highest during the time that the char surface temperature is rising. After the char surface temperature has attained a steady value, the mass loss rate soon becomes constant.

The Effect of Varying the Phenolic-Nylon Formulation

Protection time.- The temperature histories for the other percentage compositions of phenolic-nylon were similar to those shown in figure 3. Because the density of each composition was different, the thickness corresponding to a heat-shield weight of 3 pounds per square foot was computed for each composition. The time required for the various material thicknesses to attain a temperature rise of 300° F was determined from the curves of material thickness plotted against time similar to figure 4. These protection time values are plotted in figure 8 by using the percentage composition of phenolic and nylon as the abscissa. Included on this curve are the data for the 100-percent phenolic and 100-percent nylon specimens. Of the phenolic-nylon compositions tested in this investigation, the 40-60 composition provided the greatest protection time. However, the peak in the curve connecting the test points representing the various combinations occurs between the 30-70 and 35-65 phenolic-nylon compositions. This peak, however, may be considered true only for the environment of the 2,500-killowatt arc jet. Similar curves were drawn for other values of temperature rise and other values of heat-shield weight, and these curves peaked at the same composition shown in figure 8. The char-thickness curve shown in figure 8 is discussed later.

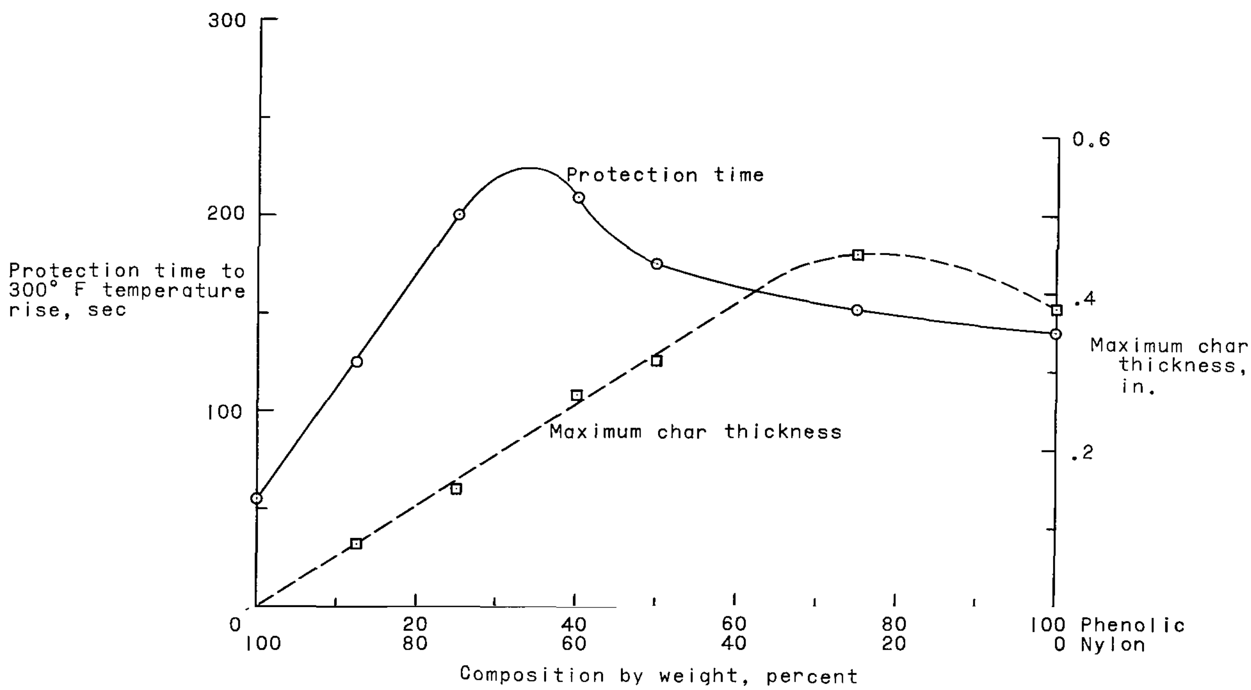


Figure 8.- Effect of composition on the protection time and maximum char thickness of molded phenolic-nylon. Protection time based on heat-shield weight of 3 pounds per square foot.

Char thickness.- Measurements of the sectioned specimens, given in table I, are plotted for four compositions in figure 9. The effect of the increasing nylon percentage is evident in the accelerated ablation rates and the diminishing char thickness. This effect can be observed further in figure 10 which shows photographs of the sectioned specimens following a 1-minute exposure in the arc jet.

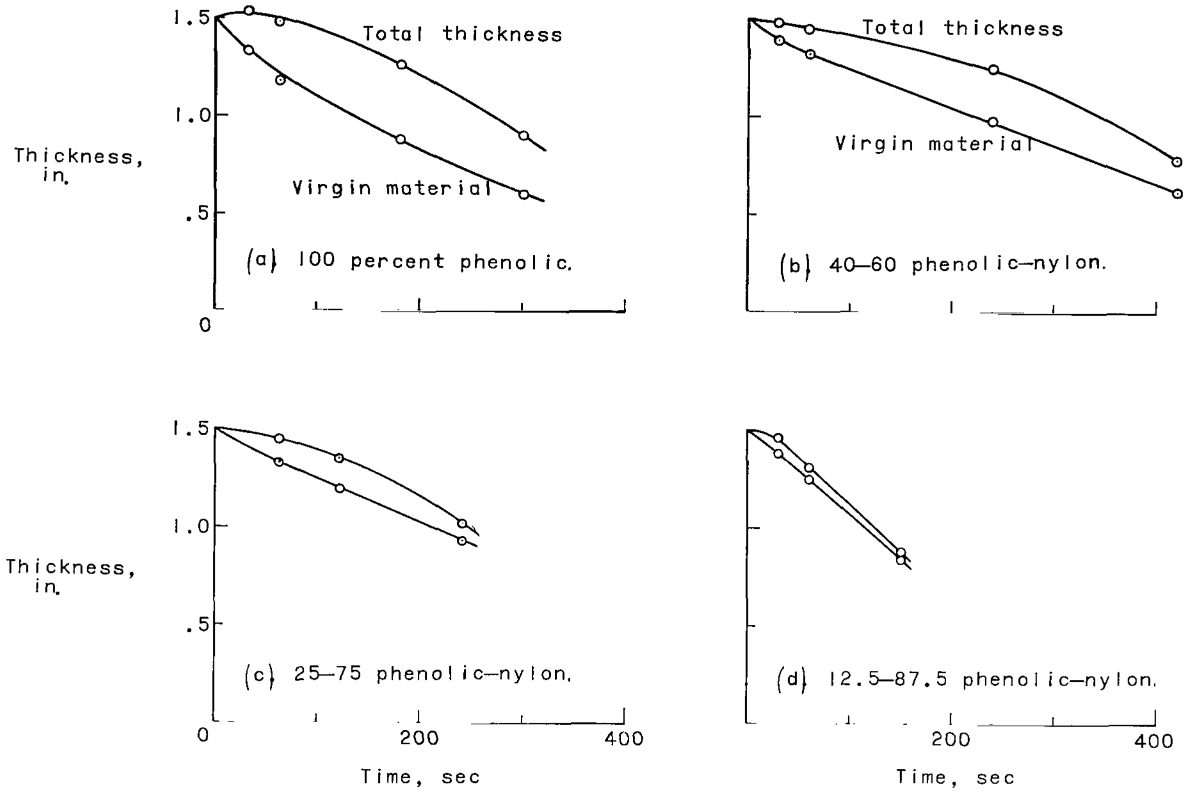
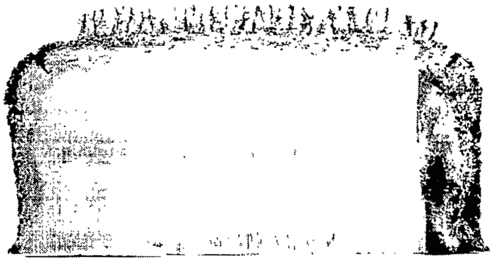


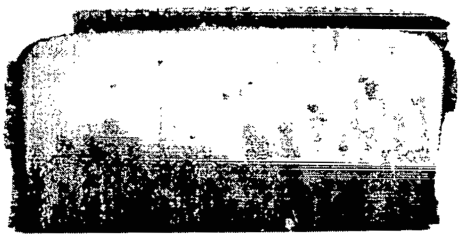
Figure 9.- Effect of phenolic-nylon composition on the ablation rate and char thickness.

The char-thickness variation with exposure time for the various compositions is shown in figure 11. As in the case of the 50-50 phenolic-nylon, the char thicknesses increased with exposure time for each composition, attained a maximum value, and then decreased. The char thicknesses are greater for those specimens having a higher phenolic percentage. The maximum char thickness attained with each composition is shown by the dashed curve in figure 8. It is readily observed that a thick char is not required to produce maximum protection in the test environment. For the compositions giving the maximum protection time, the char thickness of 0.2 inch is less than one-half of the maximum char thickness obtained in this series of specimens.

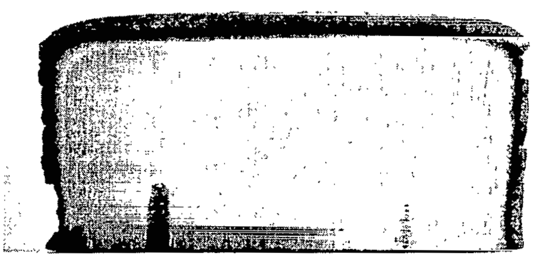
Character of char.- The character of the char structure also varied with the percentage composition of phenolic-nylon. Figure 12 shows enlarged photographs of the chars for several of these compositions. The chars in general are of a columnar structure similar to that of the 50-50 phenolic-nylon observed earlier. In the 100-percent phenolic (figs. 10(a) and 12(a)) and the 75-25 phenolic-nylon, the char columns appeared to be poorly adhered to each other, and the char structure was extremely fragile. In two cases the char on the 100-percent phenolic specimens popped off while the tested specimens sat on the shelf after the test.



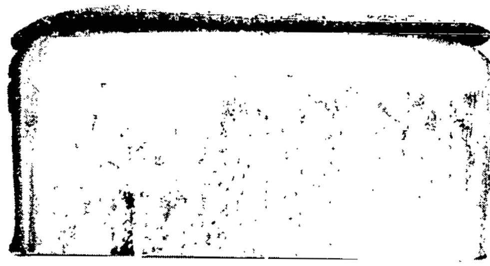
(a) 100-percent phenolic.



(b) 50-50 phenolic-nylon.

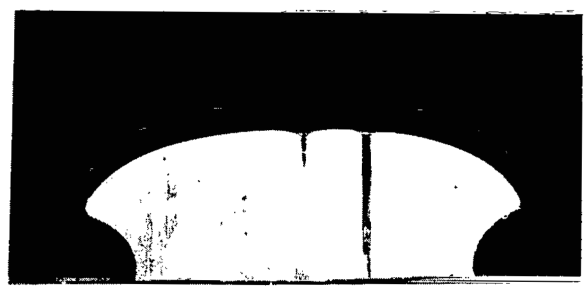


(c) 40-60 phenolic-nylon.



(d) 25-75 phenolic-nylon.

(e) 12.5-87.5 phenolic-nylon.



(f) 100-percent nylon.

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Figure 10.- Variation of char depth with phenolic-nylon composition. Specimen exposure time, 1 minute.

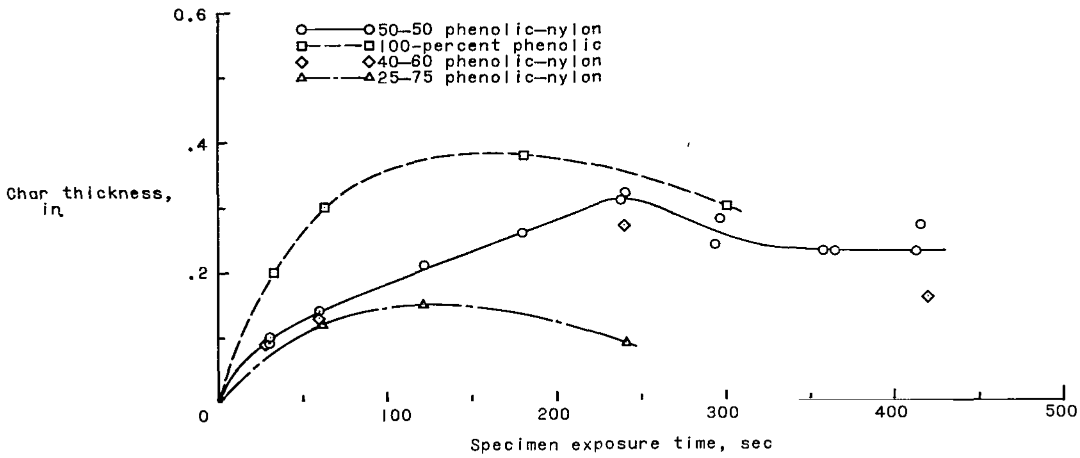


Figure 11.- Variation of char thickness with specimen exposure time for several compositions of phenolic-nylon in the 2,500-kilowatt arc jet.

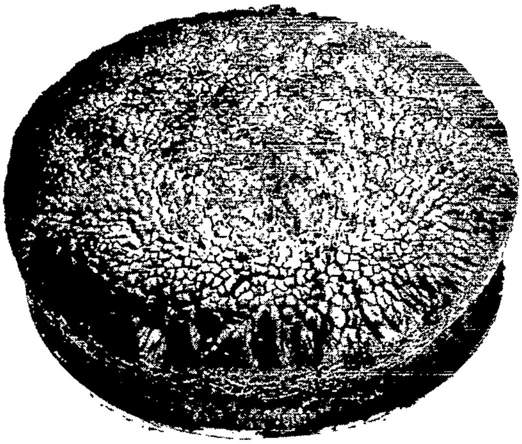
In the 50-50 (figs. 10(b) and 12(b)) and 60-40 phenolic-nylons the char appeared to be contiguous and, although brittle, could be handled in one piece. As the nylon percentage was increased, the char became thinner, and in the 12.5-87.5 phenolic-nylon (figs. 10(c) and 12(c)), the char was thin and flaky. Figure 12(d) will be discussed subsequently.

Based on the protection time afforded and on the char structure developed in the subsonic environment of the 2,500-kilowatt arc jet, the combination of phenolic-nylon providing the maximum heat-shield performance appears to be approximately 33-percent phenolic and 67-percent nylon, or simply, 1 part phenolic resin to 2 parts nylon.

The Effect of a Low-Density Filler

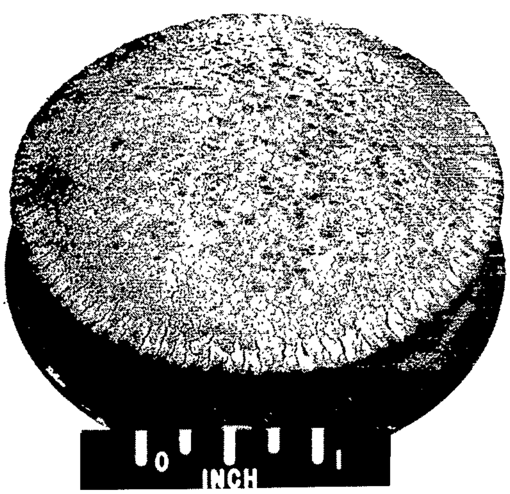
To decrease the density of the phenolic-nylon, a series of specimens was molded in which half of the powdered phenolic resin was replaced by phenolic Microballoons. This material, 25, 50, and 25 percent by weight of phenolic, nylon, and Microballoons, respectively, had a density of 40 pounds per cubic foot compared with that of 74 pounds per cubic foot for the basic 50-50 phenolic-nylon.

Protection time.- The temperature histories for the phenolic-nylon-Microballoon material were of the same character as those shown in figure 3 except that, for a given material thickness, the time to attain a 300° F temperature rise was much shorter for the Microballoon-filled material. Again, because the weight of material required is more significant than the thickness, the densities of the materials were taken into consideration, and the thicknesses corresponding to heat-shield weights of 1/2, 1, 2, 3, 4, 5, and 6 pounds per square foot were computed as far as possible. The protection time values for a 300° F temperature rise corresponding to these heat-shield thicknesses were read from the curve shown in figure 4 and a similar curve for the material containing Microballoons, and were plotted against the heat-shield weight in figure 13.

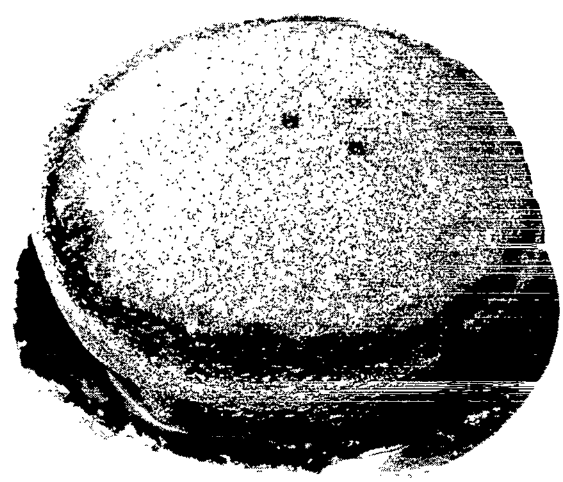


(a) 100-percent phenolic; 3 min.

(c) 12.5-87.5 phenolic-nylon; 1 min.



(b) 50-50 phenolic-nylon; 5 min.



(d) 25-50-25 phenolic-nylon-Microballoons; 2 min.

Figure 12.- Variation of char surface with phenolic-nylon composition. L-63-4783

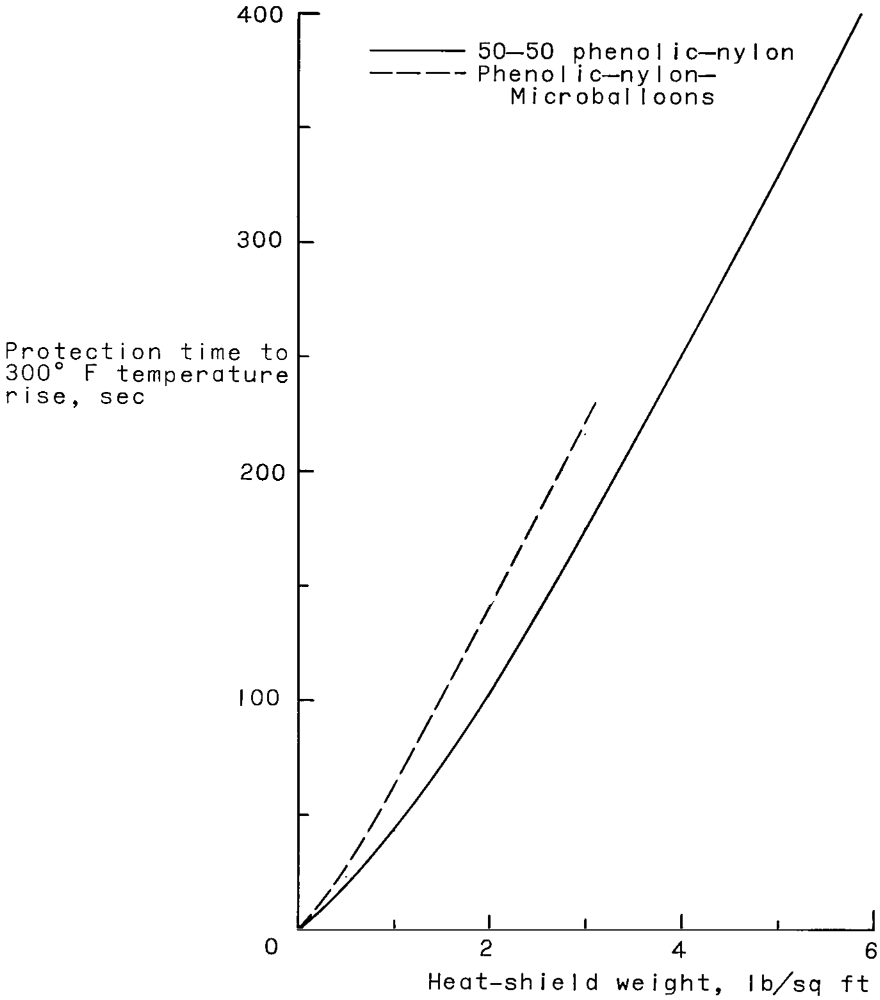


Figure 13.- The effect of Microballoons on the protection time to a 300° F temperature rise for equal weights of thermal protection material.

At a heat-shield weight of 3 pounds per square foot, the material containing the Microballoons provided 27-percent greater protection time than the 50-50 phenolic-nylon.

The curves shown in figure 13 and the screening data presented in reference 1 are based on an arbitrarily chosen temperature rise of 300° F. In order to compare the performance of these materials in applications which require less or more stringent thermal-protection requirements, that is, higher or lower allowable temperatures, respectively, the heat-shield weights and temperature history data are plotted as shown in figure 14 for two exposure times. Shown in this figure are curves for the 50-50 and 40-60 phenolic-nylon and the Microballoon-filled material. Where it is necessary to maintain a low temperature rise (20° to 500° F), the phenolic-nylon with Microballoons provides the lowest heat-shield weight. This advantage appears to decrease with increasing temperature limits and the 40-60 phenolic-nylon and the Microballoon-filled materials appear to have the same performance at temperature rises above 500° F.

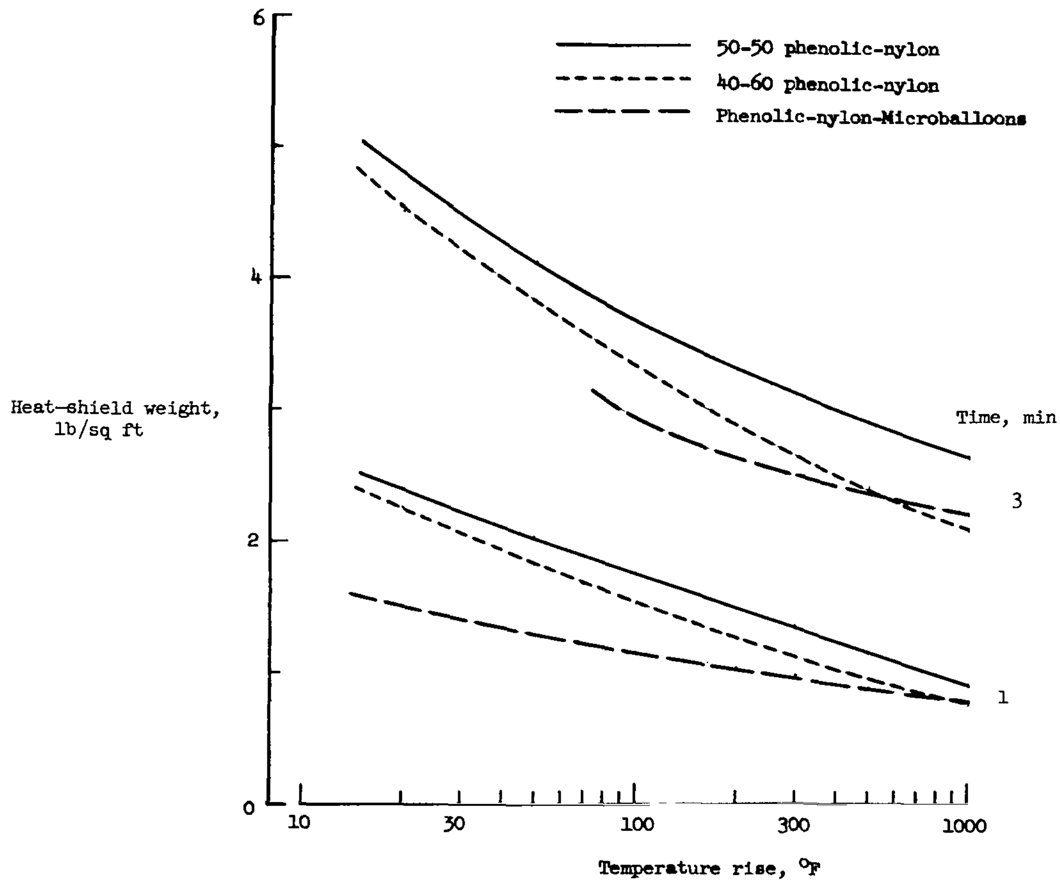


Figure 14.- Heat-shield weights required to limit the back surface temperature rise for phenolic-nylon and phenolic-nylon-Microballoons.

Char thickness.- The thickness measurements determined from the sectioned Microballoon specimens are shown in figure 15. By comparing figures 15 and 5, it

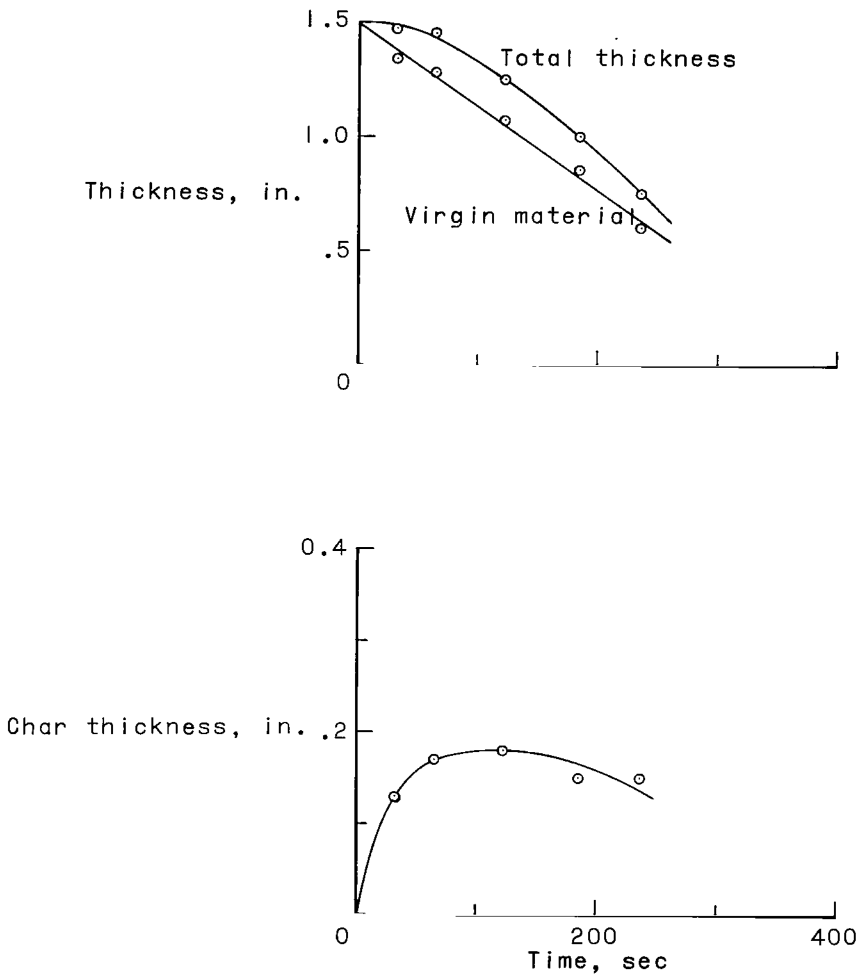


Figure 15.- Ablation and char-thickness histories for molded phenolic-nylon-Microballoons.

is noted that for the material containing Microballoons the char surface and the virgin interface receded at a higher rate than the 50-50 phenolic-nylon. Furthermore, it did not develop as deep a char as did the 50-50 phenolic-nylon; the maximum char thickness was less than 0.2 inch. To observe the surface regression more closely, the 16-mm motion-picture films of several of the longer time tests were analyzed. Typical stagnation-point regression histories are plotted in figure 16. The solid line and the dashed line representing the 50-50 phenolic-nylon and the Microballoon-filled material, respectively, are typical of nearly all the materials tested in this investigation in that two rather distinct regression rates appear. An independent check of the motion-picture film revealed that the break in these regression curves occurs at approximately the time when no further gas can be seen emanating from the surface of the ablating material. In figure 16, it is seen that the regression rate for the Microballoon-filled material is approximately twice that of the 50-50 phenolic-nylon. These higher regression rates may not be acceptable in those applications where shape changes are critical. The phenolic-nylon-refractory silica curve in figure 16 is discussed later.

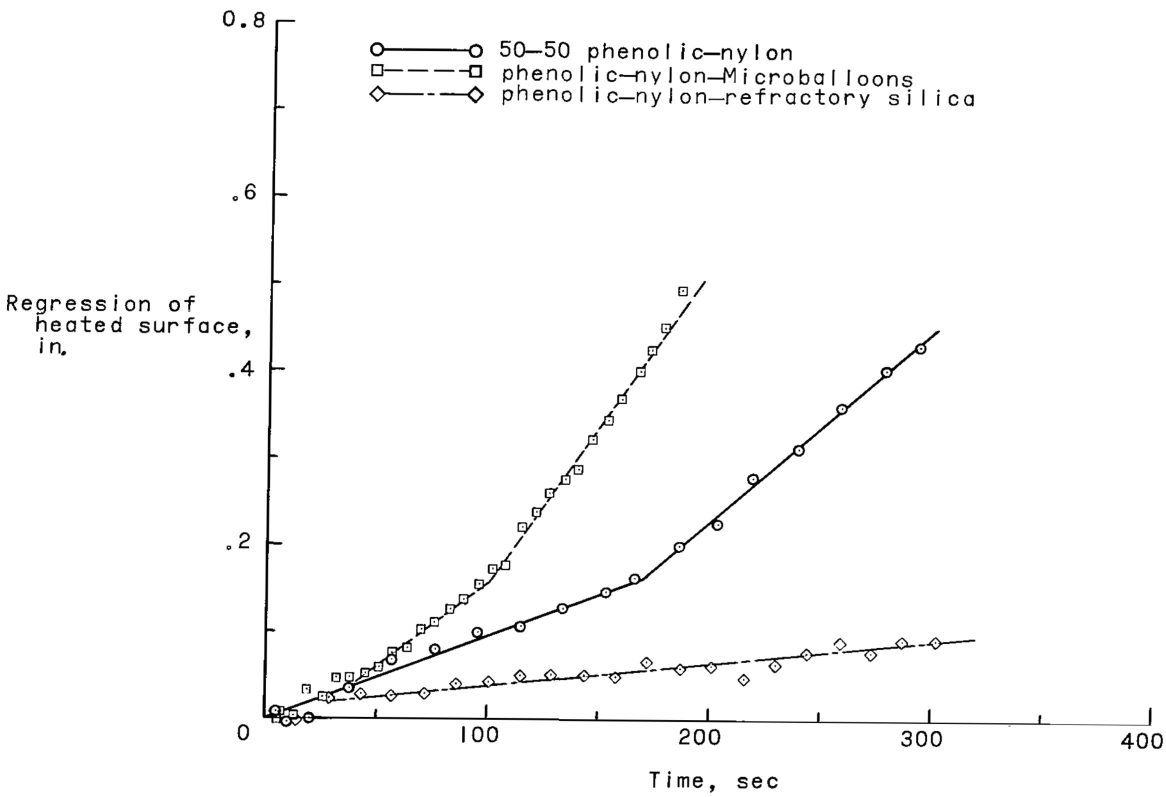
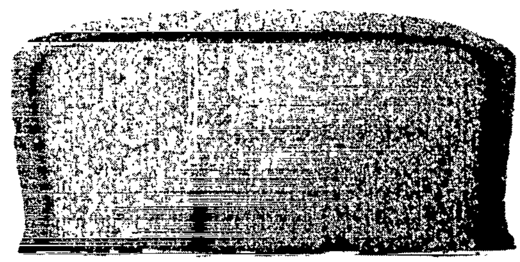


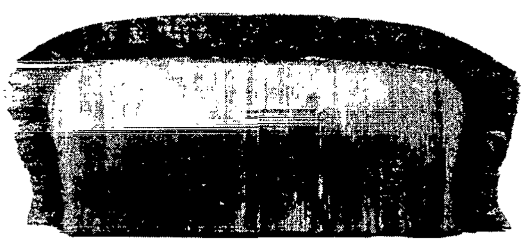
Figure 16.- The effect of fillers on the regression of phenolic-nylon.

Character of char.- The structure of the char for the Microballoon filled material is compared with that of 50-50 phenolic-nylon in figure 17 in which the 1-minute and 3-minute tests are shown. The Microballoon specimens appear to have an adherent char of good integrity. Furthermore, there appears to be no void at the interface between the char and virgin material. This condition indicates that the Microballoon filler imparts better char bonding characteristics as well

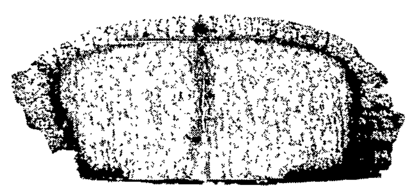
(a) 50-50 phenolic-nylon; 1 min.



(b) 25-50-25 phenolic-nylon-Microballoons; 1 min.



(c) 50-50 phenolic-nylon; 3 min.



(d) 25-50-25 phenolic-nylon-Microballoons; 3 min.

Figure 17.- Effect of Microballoons on the char structure of phenolic-nylon. L-63-4784

as decreased density to the 50-50 phenolic-nylon material. The char surface (fig. 12(d)) is similar to that of the 50-50 phenolic-nylon (fig. 12(b)).

The Effect of High-Temperature Fibrous Fillers

The discussion of the char structure formed on the 50-50 phenolic-nylon material showed that there was a strong tendency for the development of a void layer between the char and virgin material. In an attempt to improve the bond between the char and the virgin material as well as to improve the char adherency, a number of specimens were molded having high-temperature or refractory fiber fillers. The composition of these specimens was 32.5-50-17.5 percent, by weight of phenolic, nylon, and fibers, respectively. Three types of fibers were used: roving glass fibers, refractory silica fibers, and zirconia fibers. The phenolic and nylon percentages were approximately 40 and 60 percent, respectively, of the total resin weight. Addition of the glass, refractory silica, and zirconia fibers increased the density from 74 to 79, 81, and 87 pounds per cubic foot, respectively, and decreased the ablation-erosion rate of the material. By using the 1.5-inch constant-thickness specimens, test times as high as 10 minutes were possible on specimens containing these fillers.

Protection time.- The temperature histories for the fiber-filled specimens were of the same general character as those shown in figure 3 for phenolic-nylon, but the elapsed time before the steep temperature rise was greater. Again, the various densities were taken into consideration and the resulting protection times for various heat-shield weights are shown in figure 18. Based on the 300° F temperature-rise criterion, the addition of the roving glass fibers offered no improvement over the performance of the 50-50 phenolic-nylon. One reason for this apparent lack of improvement may be the high percentage of glass fibers in these specimens. This percentage is sufficient to cause a marked increase in thermal conductivity in the specimen with the resulting deterrent to heat-shielding performance. It is believed that a lower percentage of fibers may be beneficial. The refractory-silica-fiber-filled specimens showed improved performance only for heat-shield weights exceeding 3 pounds per square foot. The zirconia-fiber-filled specimens, despite their higher density, provided the longest protection time for a temperature rise of 300° F. Again, it is possible that specimens with a somewhat lower percentage of fibers, having a lower thermal conductivity, may show even better performance. (The curve for phenolic-nylon-Microballoons-refractory silica is discussed later.) To compare the performance at other temperature levels, the curves for heat-shield weight plotted against temperature rise of figure 19 are used. For a 1-minute exposure there is little difference between the four materials. For the longer exposures, however, the behavior differs. The zirconia-fiber- and refractory-silica-fiber-filled specimens show advantage, that is, lower heat-shield weight, over the 50-50 phenolic-nylon whenever the allowable back surface temperature rise is over 100° F. When a lower back surface temperature rise - below 100° F - is required, the 50-50 phenolic-nylon shows weight advantage over the fiber-filled materials. For the longest duration shown in figure 19, 5 minutes, the zirconia-fiber-filled material shows the lowest heat-shield weight.

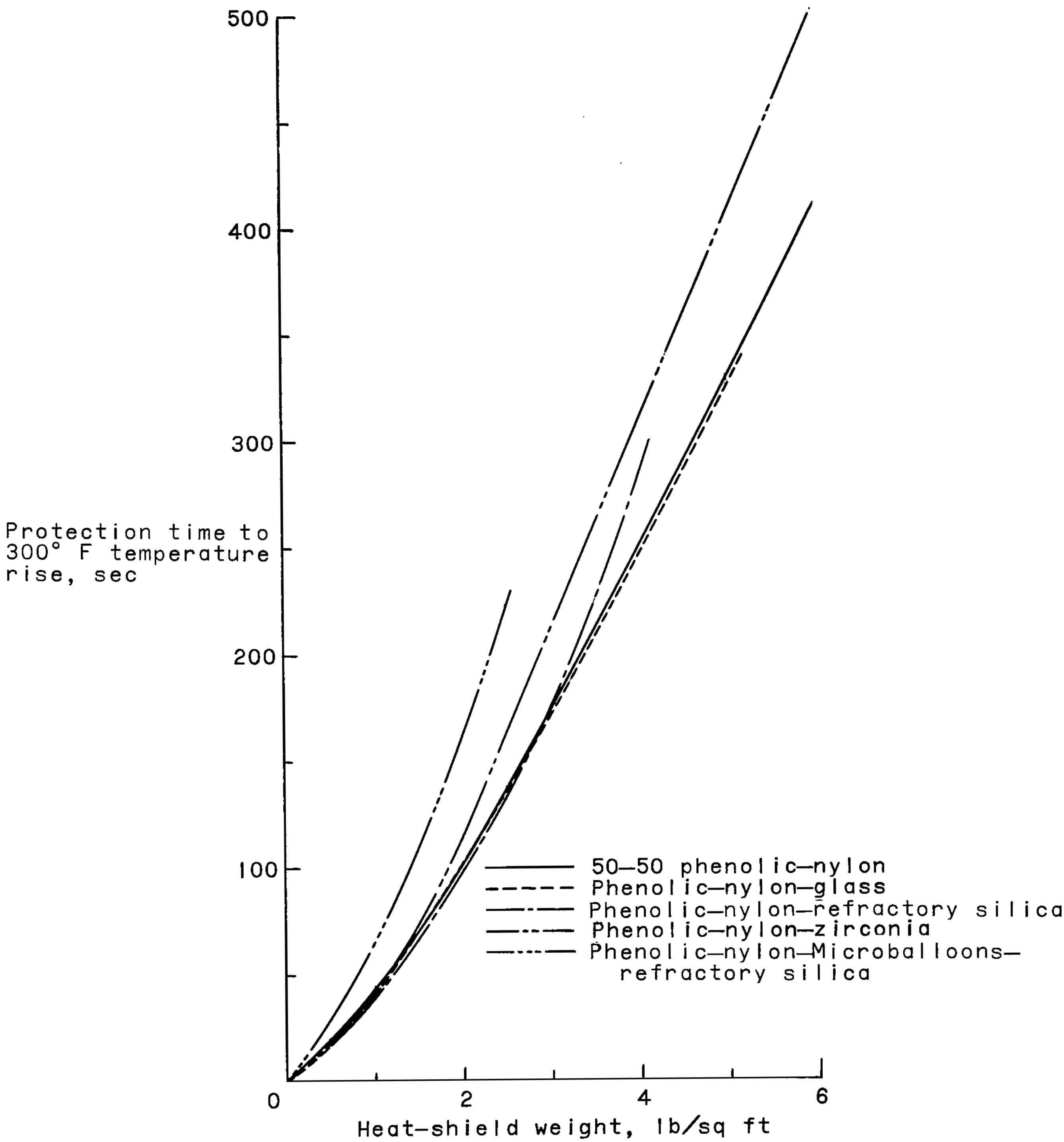


Figure 18.- The effect of high-temperature fibrous fillers on the protection time to a 300° F temperature rise.

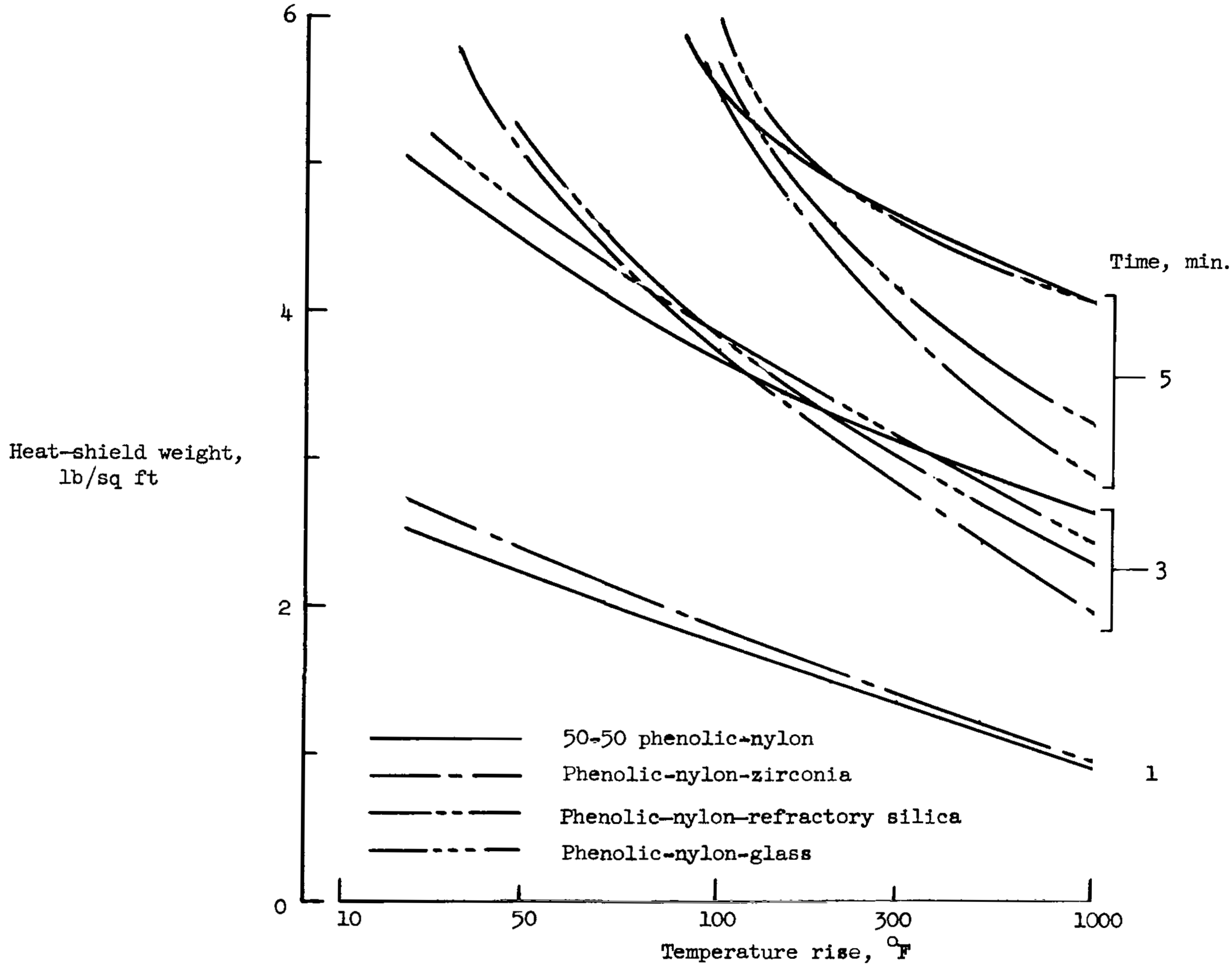


Figure 19.- Effect of high-temperature fibrous fillers on the heat-shield weight required to limit the back surface temperature rise.

Char thickness.- The thickness data for the fiber-filled materials are plotted in figure 20. Some of these curves are of different character than those observed previously. Accordingly, the char-thickness values are plotted in figure 21 for comparison with the 50-50 phenolic-nylon. Consistent with the behavior of the materials discussed previously, the char depth for the zirconia-fiber-filled specimens reached a maximum value and then decreased. The glass- and refractory-silica-fiber-filled specimens, however, developed chars which continued to increase in thickness, at least within the 400- and 600-second exposure times, respectively, of these tests. It is also noticed that the glass-fiber specimens developed a comparatively thin char whereas both the refractory-silica- and zirconia-fiber-filled specimens developed comparatively thick chars. These char thicknesses are also compared in figure 22. Figures 20(d) and 22(d) are discussed later.

Character of char.- The glass-filled specimens showed evidence of fibrous reinforcement between the char layer and the virgin material. However, there is

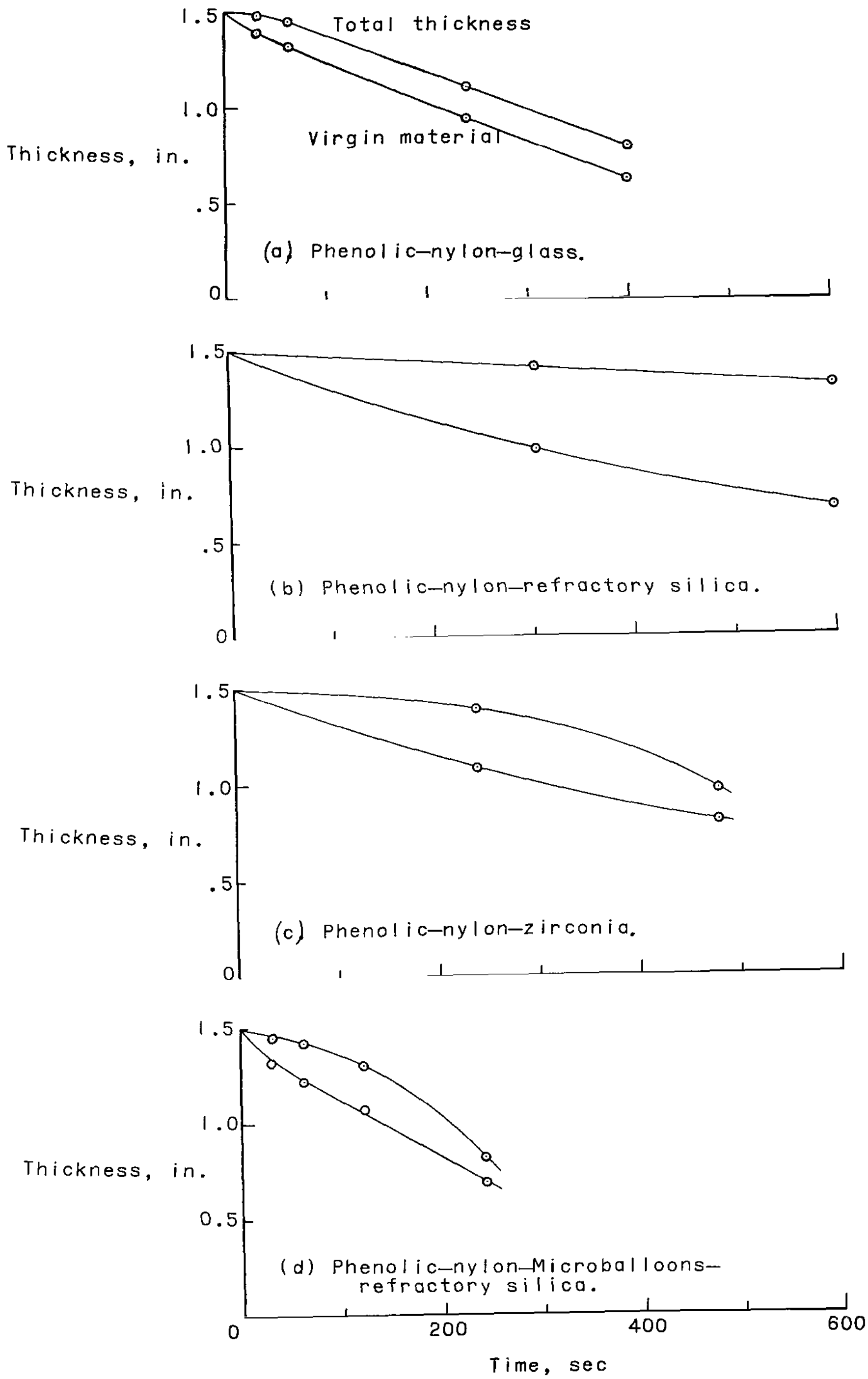


Figure 20.- Effect of high-temperature fibrous fillers on the reduction in total thickness and virgin material thickness.

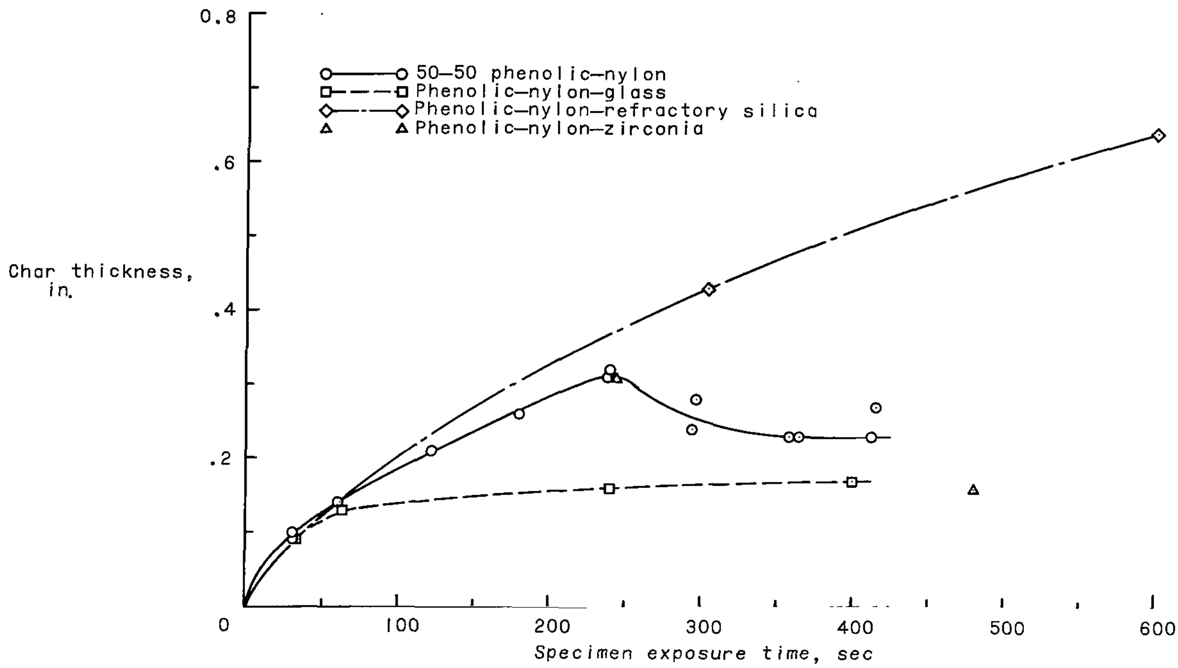
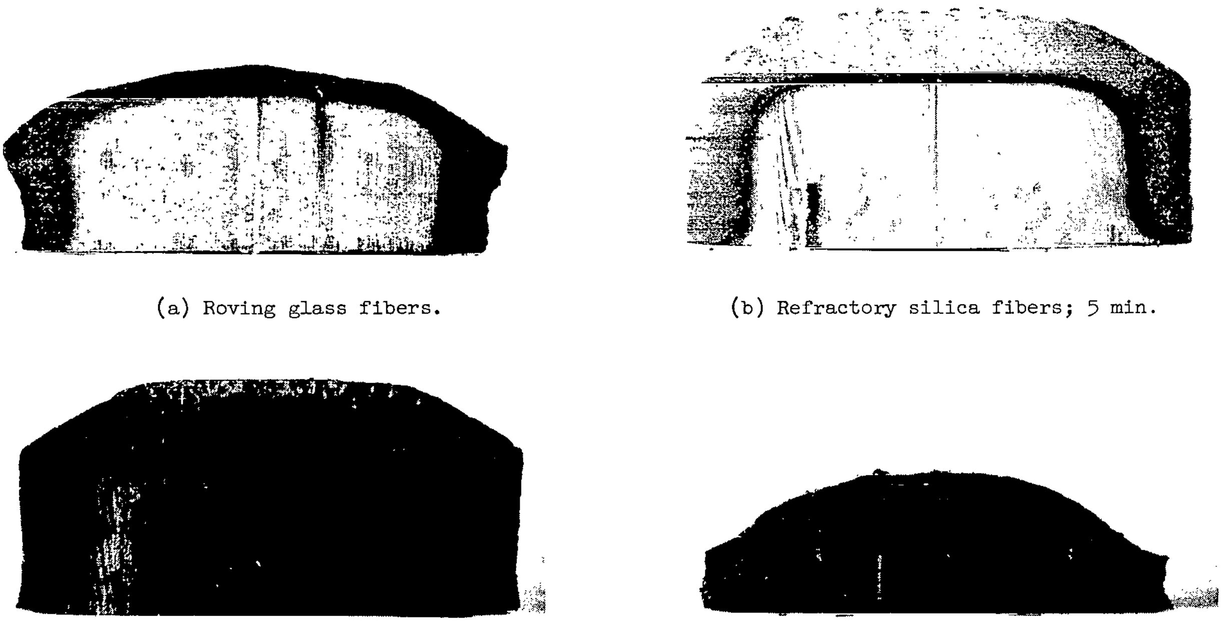


Figure 21.- Variation of char thickness with exposure time for phenolic-nylon with high-temperature fibrous fillers.

evidence of preferred orientation; that is, it appears that in the molding procedures, most of the glass fibers took on an orientation parallel to the specimen surface. The sectioned refractory-silica- and zirconia-fiber-filled specimens, however, show no evidence of discrete fibers. A review of the formulating procedure revealed, in the case of the refractory silica fibers, that the sieving and mixing operations had reduced many of these fibers to a powder. To a somewhat lesser extent the same thing had happened to the zirconia fibers. Despite the reduction of most of the fibers to dust, the superior performance of these materials, shown in figure 19, indicates that the refractory silica and zirconia may have contributed chemically as well as mechanically to the ablation behavior. Both chars, despite the apparent lack of fibrous reinforcement, were of good integrity and were lacking in large fissures or voids. (See fig. 23.) As was true of the 50-50 phenolic-nylon, however, there was some separation between the char and the virgin material. The phenolic-nylon-refractory silica specimens showed the lowest ablation rate or the least shape change of all the materials tested in this investigation. Furthermore, the regression of the heated surface determined from the motion-picture analysis, as shown in figure 16, showed just one slope of very low regression rate.

The Effect of a Low-Density Filler Plus a High-Temperature Fibrous Filler

The increased protection time provided by the low-density filler and the low regression rate and integral char provided by the high-temperature fibrous fillers,



(a) Roving glass fibers.

(b) Refractory silica fibers; 5 min.

(c) Zirconia fibers.

(d) Refractory silica fibers with Microballoons.

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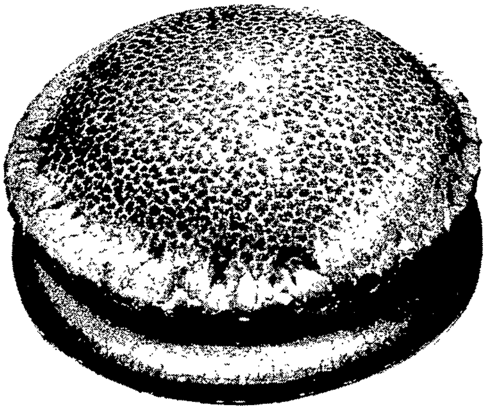
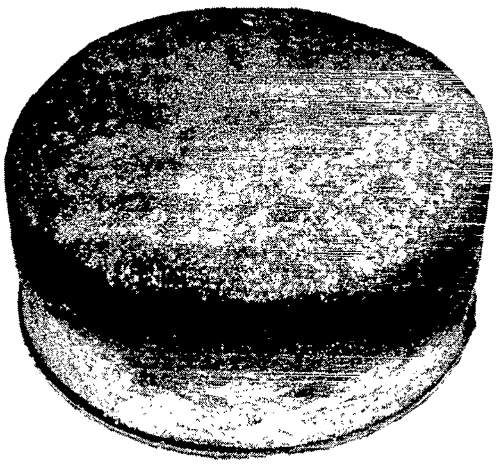
Figure 22.- Effect of high-temperature fibrous fillers on char structure. Exposure time, 4 minutes, except as shown.

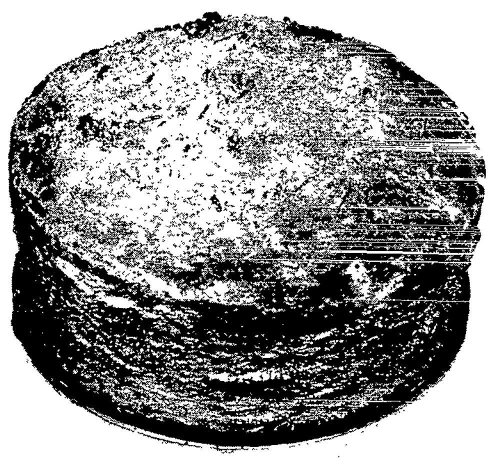


(a) 40-60 phenolic-nylon; 4 min.

(c) Phenolic-nylon-zirconia fibers; 4 min.



(b) Phenolic-nylon-roving glass; 1 min.



(d) Phenolic-nylon-Microballoons-refractory silica fibers; 1 min.

Figure 23.- Effect of high-temperature fibrous fillers on the char surface. L-63-4786

led to the molding of a composite of 22.5-45-22.5-10 percent by weight of phenolic, nylon, Microballoons, and refractory silica fibers. In formulating this composite, an attempt was made to avoid pulverizing the refractory silica fibers. This attempt was successful insofar as maintaining fiber integrity was concerned; however, there was some evidence of inhomogeneity due to occasional bunching of the fibers.

Protection time.- The temperature histories, thermocouple distances, and density of this composite were combined as before to yield the curve for the 300° F protection time plotted against heat-shield weight in figure 18. Also shown are the curves for unfilled 50-50 phenolic-nylon and the other fiber-filled specimens. The low density of this composite results in definitely improved protection time at the lower heat-shield weight. Comparison of this curve of figure 18 with the curve for the Microballoon-filled specimen of figure 13 reveals that the protection time is also increased by the refractory silica fibers. Both curves for the Microballoon-filled specimens are short, however, because the running times were limited by the comparatively higher ablation rates. To compare this composite material with the others at different temperature levels, the 3-minute exposure curves of heat-shield weight plotted against temperature rise are shown in figure 24. In this figure it is evident that the addition of both the Microballoons and the refractory silica fibers yields the lowest heat-shield weight in the 100° to 1,000° F temperature-rise range.

Char thickness.- The thickness measurements for the phenolic-nylon-Microballoon-refractory silica fiber composite are plotted in figure 20(d). Comparison of these curves with those shown in figure 15 indicates that the ablation behavior is very similar to that of the Microballoon-filled specimens without fibers.

Character of char.- By referring to the photographs in figures 22(d) and 23(d), it is seen that this composite developed an adherent char that was reasonably well bonded to the virgin material. Comparison with the refractory-silica-fiber-filled specimen, however (fig. 22(b)) indicates that the presence of the Microballoons caused a much larger ablation rate and accelerated the shape change.

Substitution of Other Low-Temperature Gasifiers for Nylon

Most of this investigation was based on a phenolic-nylon system; however, to supplement the investigation, a limited number of tests were run on specimens using other low-temperature gas producers in place of nylon. These specimens were 50-50 percent compositions of phenolic-ammonium chloride (NH_4Cl) and of phenolic-Teflon.

Protection time.- The temperature histories obtained from tests of these materials in the 2,500-kilowatt arc jet were very similar to those for the 50-50 phenolic-nylon. Because these materials had higher densities than phenolic-nylon, however, the performance based on the curves for 300° F protection time plotted against heat-shield thickness, as shown in figure 25, is inferior. When these materials are compared at temperature levels above and below 300° F, the weight advantage of the 50-50 phenolic-nylon is comparable to that shown in figure 25.

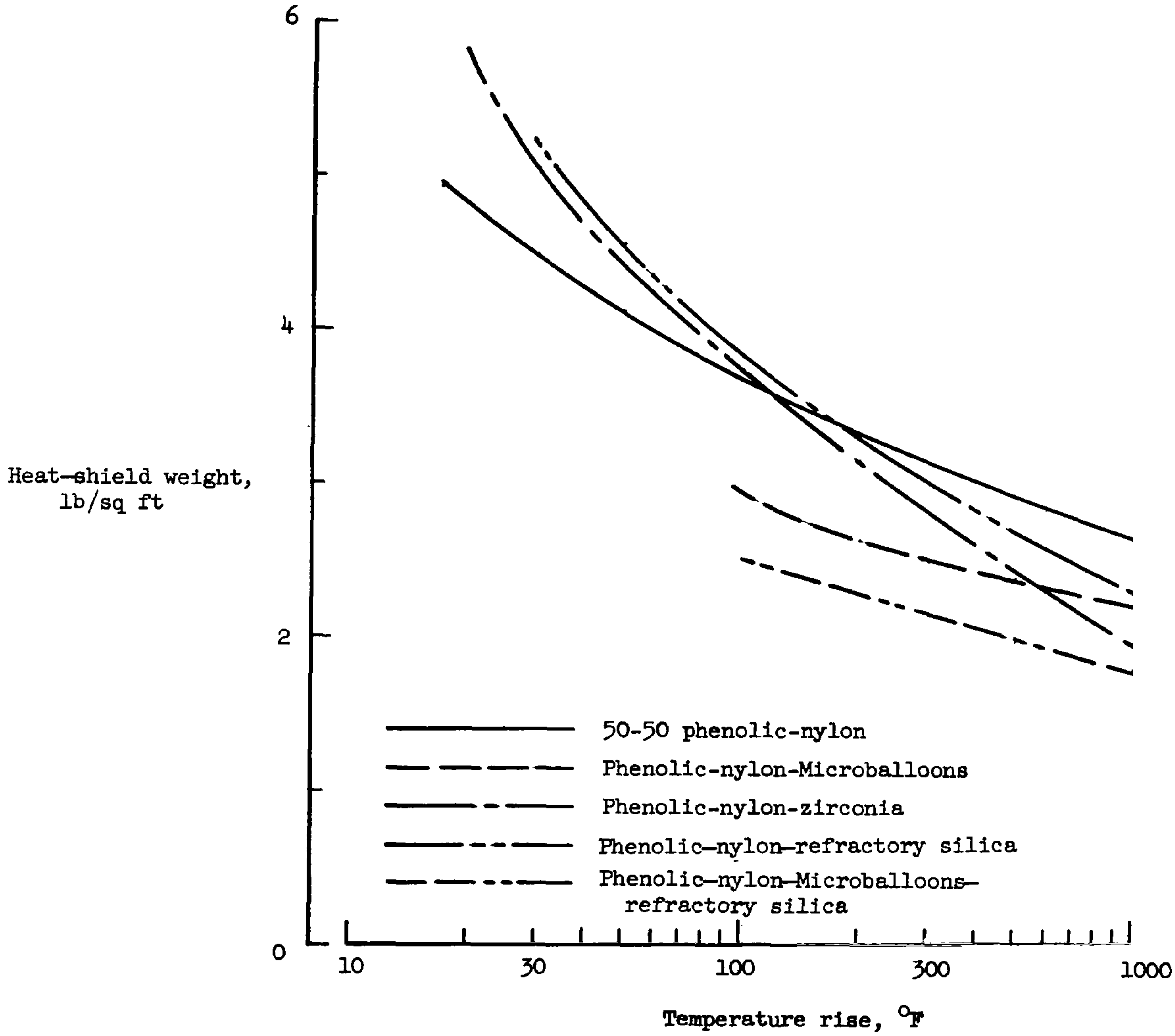


Figure 24.- Effect of Microballoons and high-temperature fibers on the heat-shield weight required to limit the back surface temperature rise for 3-minute exposure.

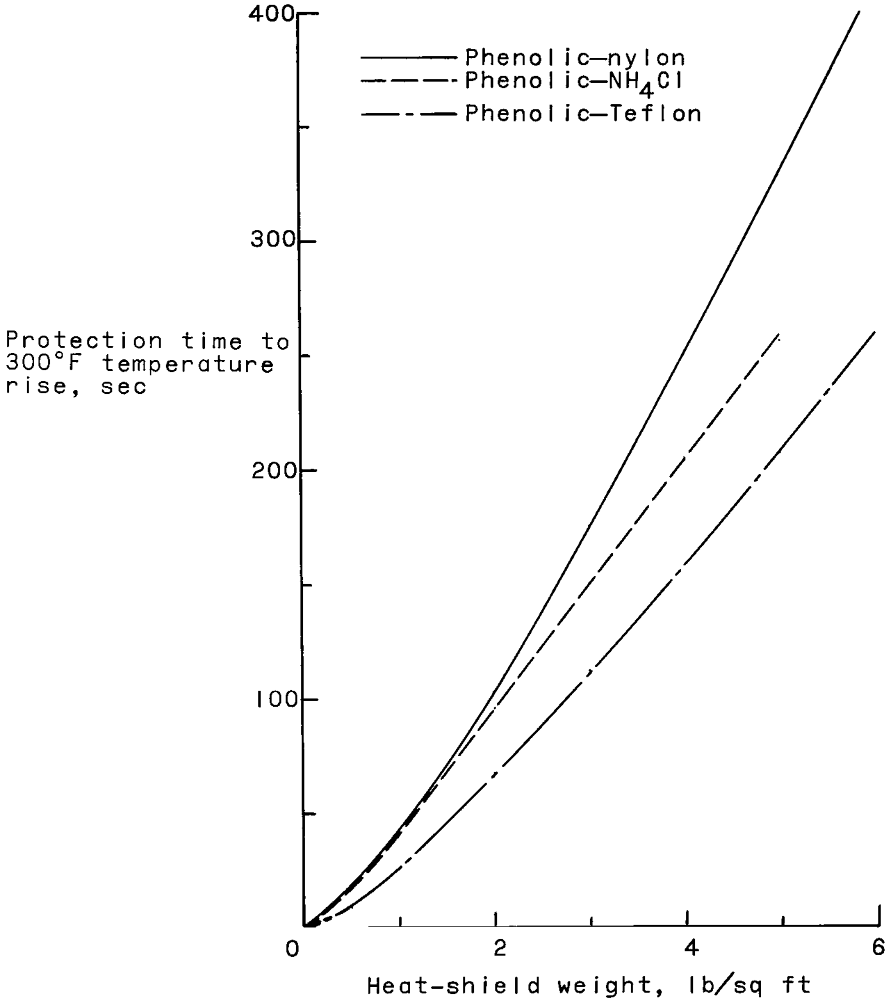
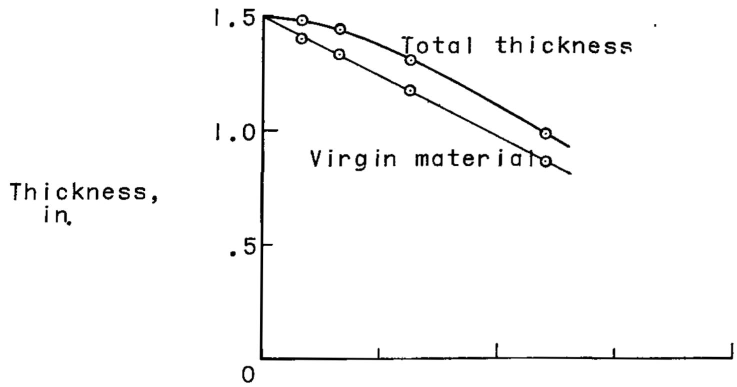
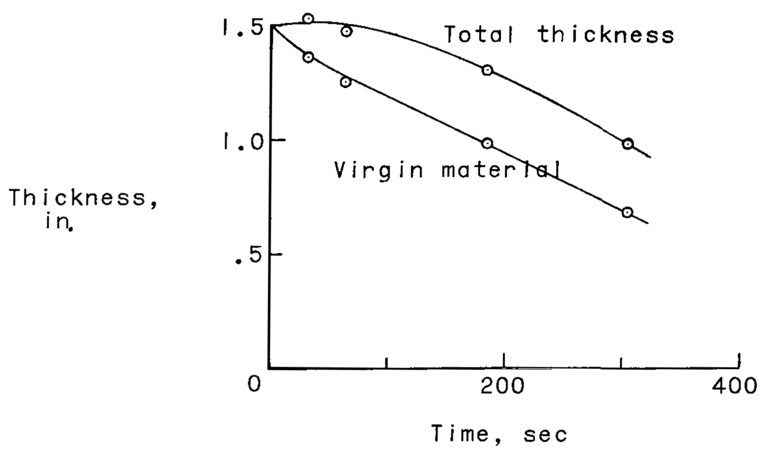


Figure 25.- The comparison of low-temperature gasifiers on the basis of protection time to a 300° F temperature rise.



(a) Phenolic-NH_4Cl.

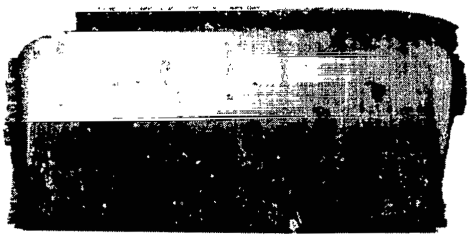


(b) Phenolic-Teflon.

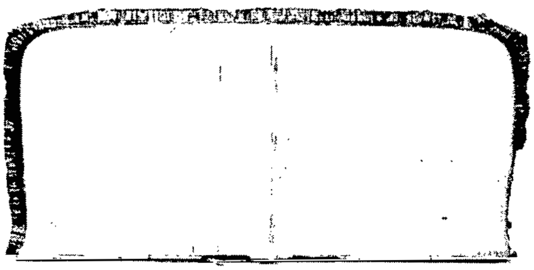
Figure 26.- Reduction in total thickness and virgin material thickness for phenolic-NH_4Cl and phenolic-Teflon.

Char thickness.- The thickness measurements of the sectioned specimens of phenolic-NH_4Cl and phenolic-Teflon are plotted in figure 26. Comparison of these curves with those for 50-50 phenolic-nylon (fig. 5) indicates that the ablative behavior based on total thickness change is about the same as phenolic-nylon. The thickness of the char formed on phenolic-NH_4Cl is much thinner than those formed on phenolic-nylon and phenolic-Teflon. These char thickness comparisons are also shown in figure 27. Sections of phenolic-nylon and phenolic-Teflon specimens exposed for 1 minute and 5 minutes are shown, and sections of phenolic-NH_4Cl specimens exposed for 1 minute and 4 minutes are shown.

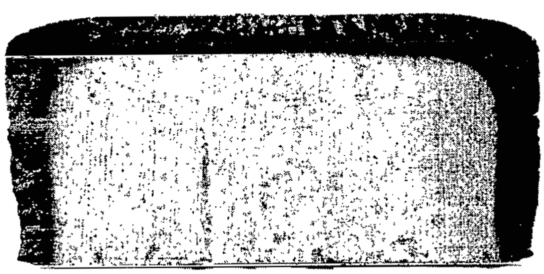
Character of char.- The character of the chars formed on the phenolic-NH_4Cl and phenolic-Teflon differed somewhat from that of phenolic-nylon. The adherence of the relatively thin char on the phenolic-NH_4Cl was similar to that of phenolic-nylon, but there was no evidence of a void between the char and the virgin material. The phenolic-Teflon developed a somewhat stronger char which also was reasonably well bonded to the virgin material. The columnar structure, however, was less adherent in the longer time tests. Most unusual was the extremely large char growth at the sides of the specimen. (See fig. 27(f).) This char growth at the sides of the phenolic-Teflon was the largest of all the specimens investigated.



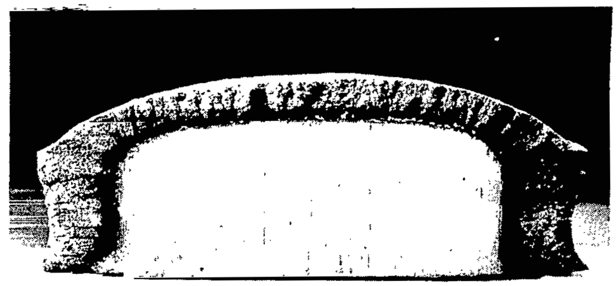
(a) Phenolic-nylon; 1 min.



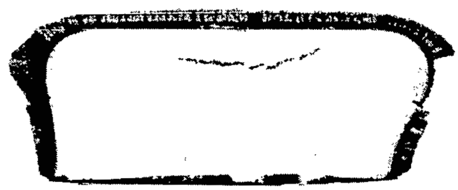
(b) Phenolic-NH_4Cl; 1 min.



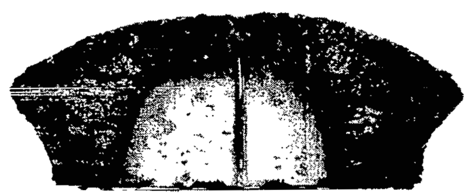
(c) Phenolic-Teflon; 1 min.



(d) Phenolic-nylon; 5 min.



(e) Phenolic-NH_4Cl; 4 min.



(f) Phenolic-Teflon; 5 min.

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Figure 27.- Photographs of sectioned specimens of 50-50 phenolic-nylon, phenolic-NH_4Cl, and phenolic-Teflon.

CONCLUDING REMARKS

The results of an experimental investigation of the thermal protection performance of a series of phenolic-based charring ablation materials in the 2,500-kilowatt arc jet at the Langley Research Center are summarized as follows:

1. For phenolic-nylon compositions there is a marked peak in performance as the proportion of phenolic to nylon is varied. For the environment of the 2,500-kilowatt arc jet the optimum ablation performance was obtained with a 1 to 2 proportion of phenolic to nylon.

2. The substitution of phenolic Microballoons for half of the phenolic resin in a basic 50-50 phenolic-nylon decreased the density of the molded material and thereby increased the thermal protection capabilities. Although the char integrity was improved, the regression rate was approximately double that of the unfilled phenolic-nylon, and more severe shape changes are inherent.

3. The use of high-temperature fibrous fillers, although it increased the density of the material, definitely improved the performance of the phenolic-nylon material as a heat shield. Char integrity was the best obtained in this series of tests, particularly where the high-temperature fibers remained to knit the char layer to the virgin material. Specimens with refractory silica and zirconia fibers showed the least shape change of all the materials tested and yielded the longest test times.

4. A composite containing phenolic Microballoons and refractory silica fibers yielded a low-density material having excellent thermal protection characteristics. In addition, a char of good integrity was produced. Dimensional changes, however, were larger than in the higher density materials.

5. The substitution of ammonium chloride or Teflon for nylon in the phenolic-based material yielded materials of higher density and inferior heat-shield performance in the environment of the 2,500-kilowatt arc jet.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., August 15, 1963.

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TABLE I.- RESULTS OF TESTS ON CHAR GROWTH SPECIMENS IN 2,500-KILOWATT ARC JET

[Heating rate to 3-inch-diameter flat face, 110 Btu/ft^2-sec; stream enthalpy, 3,000 Btu/lb; original specimen thickness, 1.5 in.]

Test	Exposure time, sec	Thickness after test, in.		
		Total	Virgin	Char
100-percent phenolic resin; density, 80 lb/cu ft				
1	33	1.53	1.33	0.20
2	63	1.48	1.18	.30
3	181	1.26	.88	.38
4	301	.90	.60	.30
75-25 phenolic-nylon; density, 72 lb/cu ft				
5	290	0.98	0.48	0.50
6	300	1.00	.60	.40
50-50 phenolic-nylon; density, 74 lb/cu ft				
7	31	1.47	1.38	0.09
8	31	1.50	1.40	.10
9	60	1.46	1.32	.14
10	122	1.39	1.18	.21
11	180	1.28	1.02	.26
12	241	1.21	.89	.32
13	238	1.27	.96	.31
14	294	1.10	.86	.24
15	297	1.11	.83	.28
16	358	.92	.69	.23
17	365	.91	.68	.23
18	416	.89	.62	.27
19	413	.81	.58	.23
40-60 phenolic-nylon; density, 74 lb/cu ft				
20	30	1.48	1.39	0.09
21	60	1.45	1.32	.13
22	240	1.25	.98	.27
23	420	.78	.62	.16
25-75 phenolic-nylon; density, 71 lb/cu ft				
24	62	1.45	1.33	0.12
25	121	1.35	1.20	.15
26	241	1.02	.93	.09
12.5-87.5 phenolic-nylon; density, 64 lb/cu ft				
27	30	1.46	1.38	0.08
28	60	1.31	1.25	.06
29	150	.88	.84	.04

TABLE I.- RESULTS OF TESTS ON CHAR GROWTH SPECIMENS IN 2,500 KILOWATT ARC JET - Concluded

Test	Exposure time, sec	Thickness after test, in.		
		Total	Virgin	Char
100-percent nylon; density, 72 lb/cu ft				
30	61	0.89	0.89	----
25-50-25 phenolic-nylon-Microballoons; density, 40 lb/cu ft				
31	32	1.47	1.34	0.13
32	65	1.45	1.28	.17
33	122	1.25	1.07	.18
34	185	1.00	.85	.15
35	236	.75	.60	.15
32.5-50-17.5 phenolic-nylon-glass; density, 79 lb/cu ft				
36	33	1.48	1.39	0.09
37	63	1.45	1.32	.13
38	240	1.10	.94	.16
39	400	.79	.62	.17
32.5-50-17.5 phenolic-nylon-refractory silica; density, 81 lb/cu ft				
40	304	1.40	0.97	0.43
41	600	1.30	.66	.64
32.5-50-17.5 phenolic-nylon-zirconia; density, 87 lb/cu ft				
42	240	1.39	1.08	0.31
43	480	.96	.80	.16
22.5-45-22.5-10 phenolic-nylon-Microballoons-refractory silica; density, 40 lb/cu ft				
44	31	1.45	1.32	0.13
45	62	1.42	1.22	.20
46	122	1.30	1.07	.23
47	242	.82	.69	.13
50-50 phenolic-ammonium chloride; density, 82 lb/cu ft				
48	33	1.48	1.40	0.08
49	65	1.44	1.33	.11
50	125	1.30	1.17	.13
51	240	.98	.86	.12
50-50 phenolic-Teflon; density, 93 lb/cu ft				
52	32	1.53	1.36	0.17
53	64	1.47	1.25	.22
54	184	1.30	.98	.32
55	304	.98	.68	.30

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